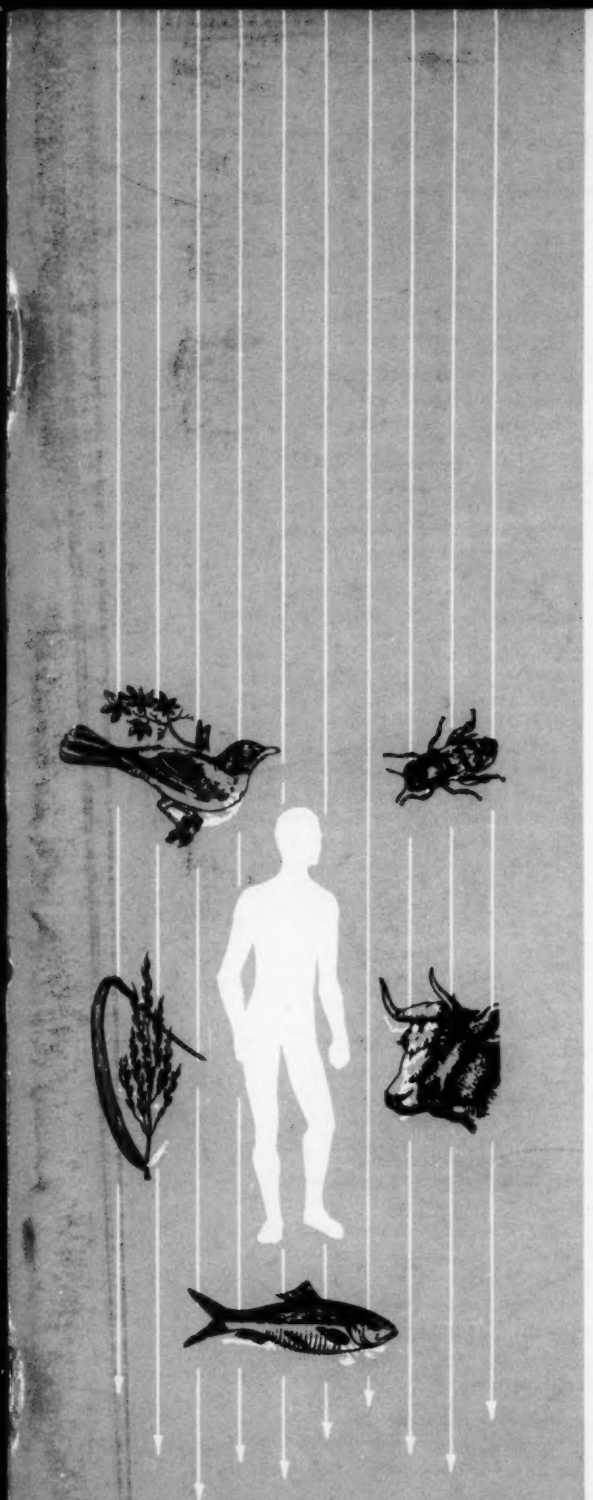

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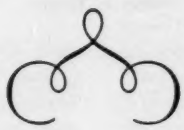

A Tribute to Sylvia O'Rear and Her Staff

Self-praise is seldom viewed with admiration. For a special reason, however, the Editorial Advisory Board feels it is appropriate to boast momentarily about the success of the *Pesticides Monitoring Journal*. Specifically, the reason is to pay tribute to Sylvia O'Rear, former *PMJ* Editorial Manager, and to members of her staff, particularly Lynn Herring and Priscilla Holman, technical editors.

As a result of recent organizational changes within the U.S. Environmental Protection Agency, the function of the Editorial Manager has been transferred from Chamblee, Georgia, to Washington, D.C. However, Mrs. O'Rear and her staff were unable to come to Washington. Because these individuals' contributions to the *Journal* have been outstanding, the Monitoring Panel and the Editorial Advisory Board unanimously decided to dedicate this issue of the *Journal* to them.

Perhaps the most fitting tribute that could be given this staff is a statement on the accomplishments of the *Journal*. Although the publication is relatively young, it has in a little over six years achieved national and international recognition as evidenced by the large number of worldwide subscribers. In addition, with each new issue of the *Journal* it becomes more evident that non-Federal sources, as well as foreign sources, are providing an increasing number of papers for publication. We believe these facts are an indication that the *Journal* has become one of stature in its field and that Mrs. O'Rear and her staff played a major role in this accomplishment.

The Monitoring Panel and the Editorial Advisory Board recognize that the Editorial Staff has been instrumental in developing and maintaining the confidence of authors and of other editorial staffs. Since the *Journal's* initial publication in June 1967, the editors have attained a high level of competence in scientific editing. Their understanding of the pesticides field has been invaluable in evaluating each manuscript and determining the extent of editing required. In spite of extensive editing on many manuscripts, the record shows that Sylvia, Lynn, and Priscilla never offended a single author but, on the contrary, almost always received praise and gratitude for their efficient manner of editing. We are confident that our readers agree that the quality of the *Journal* exemplifies the efforts of the Editorial Staff in this area.

Above all, the personal dedication of this fine staff will be missed. The Monitoring Panel and the Editorial Advisory Board commend them for a job well done and extend our best wishes.

We would be remiss if we did not acknowledge that Paul Fuschini, the new Editorial Manager, and his staff fully recognize the importance of their new role. We wish to assure *PMJ* readers and contributing authors that the Editorial Advisory Board pledges its full support to the new Editorial Staff in helping insure that the *Journal* will continue to merit the respect of the scientific community.

John R. Wessel
Chairman
Editorial Advisory Board, *PMJ*

PESTICIDES IN PEOPLE

Organochlorine Pesticide and Polychlorinated Biphenyl Residues in Biopsied Human Adipose Tissue—Texas 1969-72

James E. Burns[1]

ABSTRACT

Organachlorine pesticide residue levels were determined in 221 samples of human adipose tissue from elective surgery in 1969-72 in the lower Rio Grande Valley of Texas. Standard electron capture—gas-liquid chromatographic methods were used. The total DDT level was 23.18 ppm; the DDE level was 17.37, the highest yet reported for a general population. Dieldrin and β BHC levels were also high: 0.35 and 1.29 ppm, respectively. No decrease in storage levels during the study period was detected. There was no difference due to sex, but Mexican-Americans had significantly higher residues of DDE, p,p'-DDT, and dieldrin than did Anglo-Americans. Polychlorinated biphenyls were detected in 15 samples in 1971 but none were detected in the other 3 years.

Introduction

The presence of organochlorine pesticide residues in humans and other nontarget organisms as a reflection of high lipid solubility and unusual stability has generated much investigation. These studies have attempted to monitor temporal and geographic variations in residues (*1-14*). The effort included epidemiological investigations to define factors modifying residue levels and to detect alterations in morbidity and mortality (*3, 7, 9, 15*). This study reports organochlorine residues in adipose tissue of persons undergoing elective surgery in 1969-72 in the lower Rio Grande Valley of southeast Texas. The study area is a geographically isolated and well-defined semitropical agricultural region. It has been subjected to heavy pesticides usage, predominantly on cotton. Incidental to the investigation of pesticide residues has been the detection of polychlorinated biphenyls (PCB's). These compounds have been detected widely in the environment and in human tissue (*16, 17*). This report also includes data on PCB's in the adipose samples analyzed for organochlorine residues.

Methods and Materials

A total of 302 samples of adipose tissue of approximately 5 g each were obtained from elective surgeries performed at one local hospital in 1969-72. The samples were frozen within 30 minutes of excision and stored in glass containers with foil-lined lids at −18°C until analysis. Demographic data were obtained by chart inspection; 81 samples were eliminated because of ambiguities, inconsistencies, insufficient lipid (<30%), or nonlocal residence. It was not possible to determine a pesticide exposure history but none of the samples came from people with known unusual exposure. Extraction, cleanup, and analyses were performed in compliance with the methods prescribed for Community Pesticide Studies Laboratories (*18*). The extraction and cleanup procedures followed the modified Mills, Onley, and Gaither method (*18, 19*).

The concentrated 6% and 15% diethyl ether in petroleum ether fractions were injected into a Micro-Tek 220 gas chromatograph using a tritium foil electron-capture detector and a 6-ft-by-¼-in. outer-diameter glass column. The column contained one of two combinations: 1.5% OV-17 and 1.95% QF-1 on 100-120 mesh Chromosorb W (HP), or 4% SE-30 and 6% OV-210 on 80-100 mesh Chromosorb W (HP). Operating conditions were: column, 200° C; inlet, 225° C; detector, 205° C; carrier gas, nitrogen; flow rate, 70 ml/min; parallel plate electron capture detector operated at DC voltage to cause ½ full-scale recorder deflection for 50 pg aldrin; attenuation, 10 by 16; operating voltage, 22 v; total theoretical plates, > 3500 for each column.

[1] U.S. Public Health Service, assigned to Technical Services Division, Office of Pesticide Programs, U.S. Environmental Protection Agency, 152 East Stenger, San Benito, Texas 78586.

Quantitation was by peak height and all residues were calculated on a total extractable lipid basis. When there was any question of peak identity, thin-layer chromatography (TLC) confirmation was obtained. All 6% fractions were scanned by electron-capture—gas-liquid chromatography (EC-GLC) and TLC for PCB's and quantitated visually by TLC using Aroclor 1260 as the reference standard.

Inter- and intralaboratory quality control samples and all standards were supplied by the Primate and Pesticides Effects Laboratory, Perrine, Florida. Quality control samples were stored and analyzed with each batch of study samples and the laboratory was in control for the entire study period.

Recovery studies for all residues except PCB's were consistently above 80% and usually above 90% during the study period; residues are reported in this paper without adjustment. Recovery studies were not performed for PCB's but the method is known to have a precision of ± 50% when Aroclor 1260 is the reference standard (*18*).

The limits of detectability for the residues reported are: 0.01 ppm for heptachlor epoxide, DDE, and dieldrin; 0.02 ppm for β BHC, *o,p'*DDT, TDE, and *p,p'*-DDT; and 0.5 ppm for PCB's. Chemical names appear in the Appendix.

Results

Table 1 presents the mean level of the organochlorine residues found in adipose tissue of residents of the lower Rio Grande Valley of Texas for the study period 1969-72. Table 2 shows the percent occurrence of the same residues. In spite of the greatly decreased use of all these agents since 1968 and the abstinence, due to insect resistance, from DDT usage during the period, the level of these residues did not decrease. There are some apparently random, statistically significant variations but there are no trends.

TABLE 1.—*Mean organochlorine pesticide residues in human adipose tissue from elective surgery—Texas, 1969-72*

		Residue: ppm (mean ± standard deviation)[1]							
	No.	DDT-R [2]	DDE	*p,p'*-DDT	TDE	*o,p'*-DDT	Dieldrin	HE	βBHC
Total	221	23.18±15.36	17.37±10.90	3.48±2.54	.10±.11	.24±.28	.35±.23	.11±.11	1.23±.95
Year									
1969	26	23.04±17.50	16.50±11.86	4.12±2.56	.14±.08	.34±.23	.33±.23	.14±.09	.93±.41
1970	68	21.03±11.15	15.95±8.04	3.07±2.29	.09±.12	.10±.14 [5]	.29±.22	.08±.07 [4]	1.21±.87
1971	88	22.32±15.79	16.58±11.26	3.44±2.53	.08±.09	.32±.34	.36±.21	.14±.10 [5]	1.34±1.21
1972	39	29.29±17.35	22.52±12.10 [4]	3.08±2.75	.14±.13	.25±.27	.43±.28	.14±.13	1.20±.66
Sex									
Female	122	23.04±14.72	17.12±10.33	3.62±2.71	.10±.11	.24±.24	.35±.25	.11±.11	1.20±1.10
Male	99	23.22±16.03	17.55±11.56	3.30±2.30	.11±.11	.25±.33	.34±.20	.11±.10	1.26±.72
Ethnic [3]									
M.A.	151	25.75±16.16	19.35±11.73	3.84±2.58	.10±.12	.24±.23	.38±.22	.12±.11	1.23±1.04
Other	70	17.85±10.98 [5]	13.31±7.33 [5]	2.70±2.28 [5]	.08±.08	.24±.38	.27±.18 [5]	.11±.10	1.17±.73

[1] When $p > .01$, no notation appears; 4 values ≧ 10x the mean have been eliminated. All residues calculated on a total extractable lipid basis.
[2] DDT-R = DDT + 1.114 (DDE + TDE).
[3] M.A. = Mexican-American (Spanish surname); other = Non-Spanish surname.
[4] $p < .01$.
[5] $p < .001$ (t-test).

TABLE 2.—*Organochlorine pesticide residues in human adipose tissue from elective surgery—Texas, 1969-72*

		Percent Occurrence							
	No.	DDT-R [1]	DDE	*p,p'*-DDT	TDE	*o,p'*-DDT	Dieldrin	HE	βBHC
Total	221	100	100	100	93	81	98	98	99
Year									
1969	26	100	100	100	96	93	89	89	93
1970	68	100	100	99	90	56	99	97	100
1971	88	100	100	100	84	88	100	100	100
1972	39	100	100	100	100	97	100	100	100
Sex									
Female	122	100	100	100	97	84	97	98	99
Male	99	100	100	100	88	77	100	98	100
Ethnic [2]									
M.A.	151	100	100	100	94	88	98	99	100
Other	70	100	100	100	91	64	99	96	99

[1] DDT-R = total DDT + 1.114 (DDE + TDE).
[2] M.A. = Spanish surname; other = Non-Spanish surname.

There are no sex differences in residue occurrence, but people with Spanish surnames have higher residues (total DDT, DDE, *p,p'*-DDT, and dieldrin) than people with non-Spanish surnames ($p<0.001$). Classification by Spanish surname is used as an approximation of Mexican heritage and is certainly only an approximation of ethnic origin.

The mean sample storage intervals were 1.8 months in 1969, 6.7 months in 1970, 11.0 months in 1971, and 6.1 months in 1972. In spite of these rather marked differences there was no correlation between this variable and the residue levels. The mean ages for each year (56 for 1969, 55 for 1970, 54 for 1971, and 52 for 1972) suggest the samples were selected from the same population. There were also no differences in distribution of ethnic group, sex, or type of surgery for any of the study years.

The type of surgery from which our adipose samples were drawn is shown in Table 3. The proportion of lipid in the samples averaged 77.2%. There was no correlation between age and pesticide residues; almost all tissue samples were from adults. Previous reports have shown age correlations in only the youngest groups (*3*).

TABLE 3.—*Classification of elective surgery supplying adipose tissue—Texas, 1969-72*

Inguinal hernia	44%
Umbilical hernia	27%
Incisional hernia	13%
Hernia, other	4%
Lipoma	6%
Other types of surgery	6%
	100%

The detection of PCB's is detailed in Table 4; surprisingly, these residues appeared during one year only: 1971. This group of 15 people, compared to people not having PCB's, did not differ significantly in sex, ethnic background, sample storage time, surgical procedure, or level of pesticide residues; but they were slightly older: 62.5 years vs. 51.5 years ($p<0.01$).

TABLE 4.—*Polychlorinated biphenyls in human adipose tissue from elective surgery—Texas, 1969-72*

	Polychlorinated Biphenyls (0 = >0.5 ppm)			
	No. samples	% positive	Mean, ppm	Range, ppm
Total	221	7	0.1	0-9.9
Year				
1969	26	0	0	0
1970	68	0	0	0
1971	88	15	1.7	0.6-9.9
1972	39	0	0	0
Sex (1971 only)				
Male	42	24	2.3	0.6-9.9
Female	46	11	0.9	0.6-1.0
Ethnic Background [1] (1971 only)				
Mex.-Amer.	61	15	0.9	0.6-1.4
Anglo-Amer.	27	22	2.9	0.8-9.9

[1] By surname.

Graphic analysis of the distribution of the seven residues showed them to be skewed somewhat to the right as has been demonstrated previously (*19*). The mean is used as the measure of central tendency for comparison to previous work rather than as the rigorous application of statistical principles.

Discussion

Although use of DDT and most other organochlorine pesticides in the Rio Grande Valley was discontinued one year before this study began, the storage level did not decrease among Rio Grande Valley residents. These pesticides have been replaced by organophosphates. These findings confirm the experience of Morgan and Roan (*9*) but contradict Warnich's findings in Utah (*12*).

Duggan's food monitoring from 1965 to 1970 shows an apparent decrease in residue levels in food (*20, 21*), the major source of pesticide intake. This decrease, combined with a decrease in local use on cotton, should result in a detectable decrease in pesticide levels of human adipose, considering Morgan and Roan's (*22*) demonstration that storage levels are dependent upon continuing intake. The exact changes that may have occurred in pesticide intake via food for our study group are unknown, although it is evident from the data that no dramatic decrease has occurred.

The significant ($p<0.01$) increase in DDE levels between 1971 and 1972 is a perplexing find. There was no corresponding increase, during that year, in TDE or DDT levels as would be expected if there had been an increase in intake via food. In fact, the National Food Monitoring Program has shown that DDT levels are higher than DDE levels for almost all samples examined (*20, 21*).

The conversion of DDT to DDE in vivo has been shown to proceed slowly (*22*) and the stability of DDT levels makes this conversion to DDE unlikely.

A possible explanation for an increase in DDE levels alone could result from the discontinuation of DDT usage in the United States. This would cause an increase in the proportion of DDE, and a subsequent increase in the proportion of DDE found in human adipose. But this theory implies an increased exposure of humans to an environmental source of DDE, which seems unlikely. Further monitoring will be necessary to establish this hypothesis.

The observed differences in DDE, *p,p'*-DDT, total DDT, and dieldrin between Mexican-Americans and Anglo-

Americans probably relate to socioeconomic factors rather than to any genetic differences. This conclusion is based on two studies. Davies (*15*) has attributed increased DDT residues in blacks primarily to their lower socioeconomic status rather than to their race; it has been observed (*23*) that in the Rio Grande Valley a disproportionate percentage of the lower socioeconomic group are Mexican-American.

Since it is unlikely that Mexican-Americans consume a larger amount of animal products, which have been shown to contribute to the bulk of dietary pesticide intake (*20, 21*), the difference in residues could relate to employment, home use of pesticides, or other factors associated with lower socioeconomic status. The lack of information in this area discourages further speculation.

A comparison between the data of this report and the residue levels which have been reported previously reveals that these are the second-highest levels of total DDT (*2*) and the highest levels of DDE yet reported in a general population. The dieldrin and β BHC levels are also high but the heptachlor epoxide levels are not remarkable (*1-15, 21*).

National and international comparisons of specimens in a study of this type are subject to substantial hazards. Some specimens are from biopsies and others are from autopsies. Samples received are handled in various ways, including storage in formaldehyde, freezing in plastic, or freezing in glass. There are significant differences in analytical technique; data are reported as means, medians, and geometric means. Some data are reported on a wet-weight basis and some on extractable-lipid basis. Some authors correct for recovery, and the computation of total DDT sometimes fails to consider a difference in molecular weight of DDE and TDE. At times, the work done in these areas is not even mentioned. However, many of the laboratories generating the data cited above are operating under the same contract and quality control program as is this laboratory; comparisons with such laboratories should be valid.

The etiology of the high residues in our study group is probably intense pesticide usage necessitated by a combination of local agricultural needs and a climate favorable to insects. Exactly how exposure occurs is obscure. Reporting residues on a total extractable lipid basis tends to make our results uniformly about 20 to 25% greater than data determined on a tissue-weight basis but the variability of lipid in adipose samples (31 to 93%) makes this a reasonable correction.

The detection of PCB's in only one year is difficult to explain. The study area is mostly rural with very little industrialization and consequently few sources of PCB's. It is possible that these residues represent immigrants from industrial areas but this has not been demonstrated; as stated earlier, it was not possible to determine a pesticide exposure history of persons in this study. Analysis of all variables identified in the study fails to demonstrate any significant differences between the people with PCB residues and those without, except that the former are slightly older: 62.5 years vs. 51.5 years ($p<0.001$).

Residue levels are in the range of those reported in the Tissue Monitoring Program (*17*) and in the Price-Welch study in Michigan (*16*) but the prevalence is certainly much lower. Without further data it must be assumed that the detection of PCB's in 1971, only, is a random event with no biological significance.

See Appendix for chemical names used in this paper.

Acknowledgments

The study was initiated by J. S. Wiseman, Ph.D. Analytical work was done by E. D. Gomes. Contributions of these and other members of the Texas Community Pesticide Laboratory are greatly appreciated.

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RESIDUES IN FOOD AND FEED

Surveys of Mercury Levels in Fish and Other Foods [1]

Robert E. Simpson,[2] William Horwitz,[2] and Caesar A. Roy[3]

ABSTRACT

The Food and Drug Administration (FDA) conducted a series of surveys of the mercury content of food in 1970, 1971, and 1972. The surveys included a wide variety of fish samples from selected freshwater regions, commercial fish from wholesale distributors, and swordfish and canned tuna fish; 10 commodities representing a high proportion of total food consumption; and 12 total diet fractions collected in the FDA continuing market basket study to determine pesticide residues in the basic 2-week diet of a 19-year-old male.

For most samples analyzed, atomic absorption was used as the determinative step; the more sensitive neutron activation technique was used to confirm low levels of mercury found by the atomic absorption method.

Swordfish samples showed the highest incidence of mercury and the average mercury content, with levels in excess of 1 ppm in more than 50% of the samples examined. Approximately 4% of the canned tuna fish contained mercury in excess of the FDA guideline of 0.5 ppm for mercury in fish. Some freshwater species contained elevated levels of mercury traceable to known sources of mercury pollution. Of other commercial fish sampled, halibut, bonita, mackerel, cod, and snapper contained some elevated mercury levels, but averaged below the 0.5 ppm guideline.

In the survey of mercury in foods in which 10 food commodities were analyzed, mercury was detected only in shrimp at levels approximating 0.05 ppm. In the total diet fractions only meat, fish, and poultry contained mercury as high as 0.04 ppm. All other fractions contained mercury levels lower than the sensitivity of the method, i.e., 0.002 ppm on a dry-weight basis.

Introduction

The toxic nature of mercury and mercurial compounds has been known for many years. Numerous instances of mercury poisonings resulting from industrial accidents have been reported, but the problem of mercury residues in foods as a result of industrial environmental contamination has been recognized only recently.

In July 1969 the Food and Drug Administration (FDA), alerted by reports of the mercury poisonings in Minamata and Niigata, Japan, resulting from environmental pollution, established an administrative guideline of 0.5 ppm for mercury in fish, shellfish, and other aquatic organisms. This guideline represents the level at which the FDA will charge that the fish is adulterated and must be removed from the market.

The FDA, assisted by study groups of scientists from within and outside the agency, has re-evaluated the guideline on at least three occasions. One study group, in its report on hazards of mercury (*1*) to the Pesticide Advisory Committee of the Secretary of the U.S. Department of Health, Education, and Welfare (HEW), concluded ". . . the interim FDA guideline of 0.5 ppm mercury in fish is, for the present, a sound basis for the protection of public health . . ."

Mercury was included as one of the toxic contaminants to be surveyed in the FDA compliance program, "Pesticide Residues—Total Diet Studies," as early as 1967 (*2*). It was also included in that program for the years 1969, 1970, and 1971.

In March 1970 FDA officials learned of a potential mercury pollution problem involving certain Canadian—American border lakes. A compliance program, "Mercury Contamination in Fish" (*3*) was initiated in April

[1] Bureau of Foods, U.S. DHEW—Food and Drug Administration, Washington, D.C. 20204.

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1970 to assess the impact of the mercury pollution on sport and commercial fish in freshwater rivers and lakes across the country.

In October of that year Jervis et al., using neutron activation analysis, reported high mercury levels in wheat, flour, and milk products in Canada (*4*). This report prompted the FDA to initiate a survey of mercury in foods (*5*) in which certain high-consumption food items were examined for mercury to obtain more information about the exposure of American consumers to mercury in the diet.

The following December, McDuffie (*6*) reported that samples of tuna examined in his laboratory showed mercury levels that exceeded the 0.5 ppm guideline. On the basis of similar findings by FDA laboratories, a joint FDA—National Canners Association (NCA) survey of mercury in tuna was initiated to examine samples from all the Nation's domestic and imported canned tuna. The survey was expanded in mid-December 1970 to include swordfish after a preliminary sampling of swordfish stocks showed a substantial number of samples that exceeded the guideline.

In January 1971, a survey of mercury in wholesale fish (*7*) was instituted to determine the extent of mercury contamination in 19 of the leading commercial fish species.

This paper summarizes results of the FDA survey programs and the various analytical methods used in examining the large numbers of samples.

Sampling and Preparation of Samples

The survey for mercury contamination in fish (*3*) initiated in the spring of 1970 included samples from the 17 FDA districts whose locations are given in Figure 1. Inspectors from each district investigated various plants engaged in the chlorine-alkali, vinyl-chloride, and other manufacturing processes which used mercury compounds. They identified the freshwater areas used for waste disposal, and collected fish from these areas. Preference was given to bottom-feeders, commercial and sport fish, and other edible fish, including predators. Whenever possible, at least six fish with a total weight of at least 1 lb were collected from each area. Mercury in the samples was determined by the district laboratory in whose territory the sample was collected.

Samples for the survey of mercury in foods (*5*) were collected by each FDA district. Two samples of the ten commodities, each weighing at least 2 lb, were obtained from local retail markets, preferably representing different manufacturers. If more than one package was required to meet the minimum weight, multiple units of

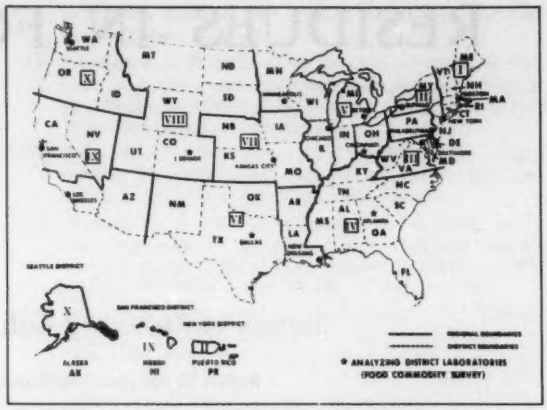

FIGURE 1.—*Food and Drug Administration districts within U.S. DHEW regions*

the same code were collected. All samples were forwarded as perishables under solid carbon dioxide by the collecting districts to one of the four analyzing districts' laboratories indicated by a star in Figure 1. The analyzing laboratories prepared composites of each commodity collected at a given district; a portion of each composite was forwarded to the FDA headquarters laboratory in Washington, D.C., for mercury determination by neutron activation analysis (NAA).

In the FDA-NCA survey of canned tuna fish and swordfish, samples were collected from warehouse stocks located in each district; samples consisted of 12 cans selected at random from different cases within a given lot.

For the survey of wholesale fish (*7*), 19 different types of other commercial fish and shellfish were sampled. Each sample consisted of five 1-lb units, each unit from a different fish, making a total of 5 lb for each lot. For shellfish, the square root of the number of containers in the lot was sampled; a minimum of 5 and a maximum of 15 subdivisions were taken. Each subsample consisted of at least 1 lb. The shellfish sampling procedure was also used for packaged fish: fresh, frozen, or processed. Each subsample contributed equally to a single thoroughly mixed slurry for analysis which was representative of the lot.

The Total Diet program (*8*) of FDA is a continuing market basket study in which 117 food items are collected and composited into 12 commodity groups for analysis. The program is intended to represent the 2-week diet of a 15- to 20-year-old male in each of the four regions of the country (Fig. 1) in which the samples are collected: Northeastern (I and II), Southern (III, IV, and VI), Central (V and VII), and Western (VIII, IX, X). The details of the selection, collection, preparation, and compositing of the samples are described in

references *8* and *9*. The homogenized, slurried composites of each commodity group were divided into 100-g portions and kept frozen until analyzed by the Kansas City District laboratory. In addition, portions of each commodity group were forwarded to the FDA headquarters laboratory in Washington for mercury analysis and multi-element screening by neutron activation techniques.

Analytical Methods

Originally the dithizone method of the Association of Official Analytical Chemists (AOAC) (*10*) and the cold vapor atomic absorption method of the Fisheries Research Board of Canada (*3*) were used to analyze fish for mercury. When the results of the collaborative study conducted by Munns and Holland (*11*) became available in late 1970, all subsequent analyses were made by their modification of the basic cold vapor atomic absorption method. The very low levels of mercury in foods other than fish necessitated the use of the more sensitive neutron activation method of evaluation.

DITHIZONE METHOD

The official final action AOAC method (*10*) consists of a nitric-sulfuric acid digestion under reflux to avoid loss of mercury. The mercury is isolated by dithizone extraction, any interfering copper is removed, and the mercury dithizonate is determined spectrophotometrically. Extreme care is required to achieve complete digestion, or results will be low. The practical limit of detectability is about 0.05 ppm. Recoveries by this method at levels of 0.2 ppm or greater ordinarily are above 90%.

ATOMIC ABSORPTION METHODS

The original Canadian method of analysis involved sulfuric acid dissolution of the sample, cold permanganate oxidation, reduction and volatilization of the mercury, and reading in a vapor-flow cell. The current first action AOAC modification of this method (*11*) utilizes a nitric-sulfuric-perchloric acid digestion under reflux, reduction and volatilization, and reading in a vapor-flow cell. The practical limit of quantitative results with this method is about 0.02 ppm. Recoveries of mercury added to fish are about 80% at the 0.5 ppm level, with a coefficient of variation of about 15% (*11*). The average and standard deviation obtained by 17 FDA laboratories for a ground, composited, reference sample of canned tuna, oil packed, was 0.34 ± 0.05 ppm; the coefficient of variation was 15%, about the same as the collaborative study value (*11*).

RADIOCHEMISTRY METHODS

Older laboratories which at some time have utilized open containers of mercury, such as barometers and leveling bulbs, or any laboratory in which thermometers, calibrating equipment, or bottles of mercury have been spilled or broken may experience low levels of mercury contamination from hidden sources. The extreme sensitivity of neutron activation analysis therefore required special preparation techniques.

All samples were prepared in a mercury-free clean room. Following irradiation, all sample vials were decontaminated of any possible extraneous radioactive mercury prior to radiochemical processing.

The sulfide precipitation method adapted by Tanner *et al.* (*12*) from that developed by R. E. Jervis (*4*) was used to process all samples analyzed in the foods survey program. Sjöstrand's electrolytic method (*13*) as modified by Heitzman and Simpson (*14*) was also used to obtain comparative values with other methods on a limited number of selected samples.

The mercury content of the samples was determined by assaying the ^{203}Hg activity using the techniques of gamma ray scintillation spectrometry.

Following a radiochemical separation, the sensitivity of neutron activation analysis for mercury is about 0.002 ppm for dry samples and about 0.001 ppm for freeze-dried samples calculated to the original wet-weight basis. All results were corrected by the individual recovery factor for the specific determination. The average recovery factor was 88%. All results on freeze-dried samples were recalculated to the original wet-weight basis.

Results and Discussion

COMPARISON OF METHODS

A number of samples which had been analyzed by several other laboratories were available for comparative analyses. Although some results of this study have been reported elsewhere (*12*, *14*), for the sake of completeness they have been included in Table 1 with additional data. The concurrence of results between neutron activation analyses and atomic absorption methods, which measure total mercury, and the gas-liquid chromatographic (GLC) analyses, which measure only methyl mercury, indicates (a) that most of the mercury in the shrimp and two pike samples is present as methyl mercury, and (b) that mercury is not lost in freeze drying.

The electrodeposition method yields mercury of high purity deposited on gold, and the results are in good agreement with those by the other methods. This technique, however, is not practical for processing the large number of samples handled in these surveys.

The results in Table 1 show remarkably good agreement by the various laboratories utilizing their individual

techniques. In all cases, special care undoubtedly was taken to insure the reliability of the reported values.

FISH SURVEY

A survey was initiated by the U.S. Department of the Interior—Federal Water Quality Administration (FWQA: a predecessor of the present U.S. Environmental Protection Agency—Air and Water Programs). J. R. Harlan, Conservation Consultant to FWQA, sent an inquiry to all State directors of fish, game, and conservation, soliciting information on the status of mercury pollution of natural resources under their jurisdictions (*15*). Results reported by the States are given in Table 2. Of the 45 States who responded to the inquiry, 13 reported levels of mercury in fish in excess of 0.5 ppm; at least six States reported levels higher then 4 ppm in some samples. Closures of fishing areas and/or warnings against eating fish from these polluted areas were issued by 16 of the States covered in the survey.

In Lake Erie (Table 3) over 20% of the fish sampled by FDA in 1970 contained mercury in excess of the 0.5 ppm guideline; over 50% of the fish from Lake St. Clair in nearly Ontario Province, Canada, were above this level. Of these, 20% showed more than 1 ppm mercury. Fish from other regions, except for Lake Ontario, had residues well below this level. For comparison, the mercury contents of fish from two Far Western areas are also listed in Table 3. More than 60% of all samples analyzed contained less than 0.1 ppm mercury. The official dithizone method of the AOAC (*10*) was used to analyze most samples collected in this survey. After adoption of the Munns and Holland method (*11*), about 60% of the Lake Erie samples were analyzed by atomic absorption. Results for the fish from Lake Erie and Lake St. Clair confirm the earlier Canadian findings: walleye, sheepshead, catfish, white bass, smallmouth bass, some perch, and carp contained the highest levels of mercury.

Other data from the FDA survey of mercury contamination in fish are given in Table 4. Of 29 freshwater areas listed, only 13 had fish containing mercury in excess of the 0.5 ppm guideline; of these, only 9 areas had fish containing more than 1 ppm. Samples from all other areas contained less than 0.5 ppm mercury.

The 1971-72 results for 13 different types of fish are shown in Figure 2. Of all the samples collected from various parts of the country, 40% (16 of 40 samples) contained levels of mercury in excess of 0.5 ppm. As illustrated in Figure 3, similar results were observed for imported freshwater fish. In this case about 45% (7 of 16 samples) contained more than 0.5 ppm.

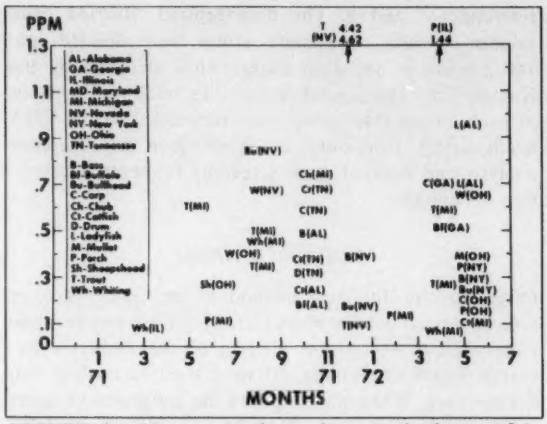

FIGURE 2.—*Mercury levels in domestic freshwater fish, 1970-72*

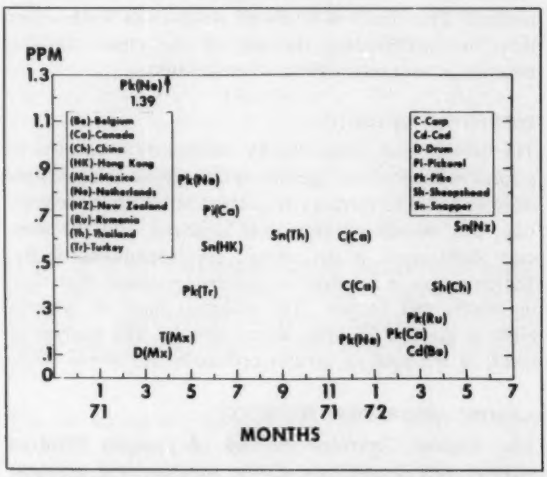

FIGURE 3.—*Mercury in imported freshwater fish, 1970-72*

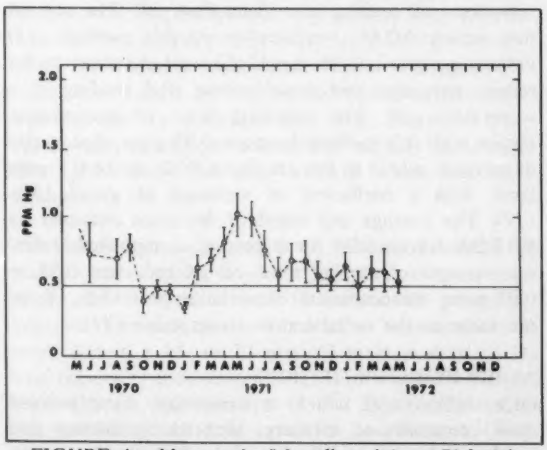

FIGURE 4.—*Mercury in fish collected from Pickwick Reservoir, Tennessee Valley Authority*

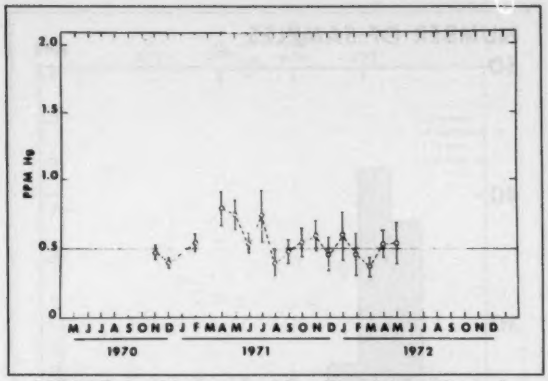

FIGURE 5.—*Mercury in fish collected from Kentucky Reservoir, Tennessee Valley Authority*

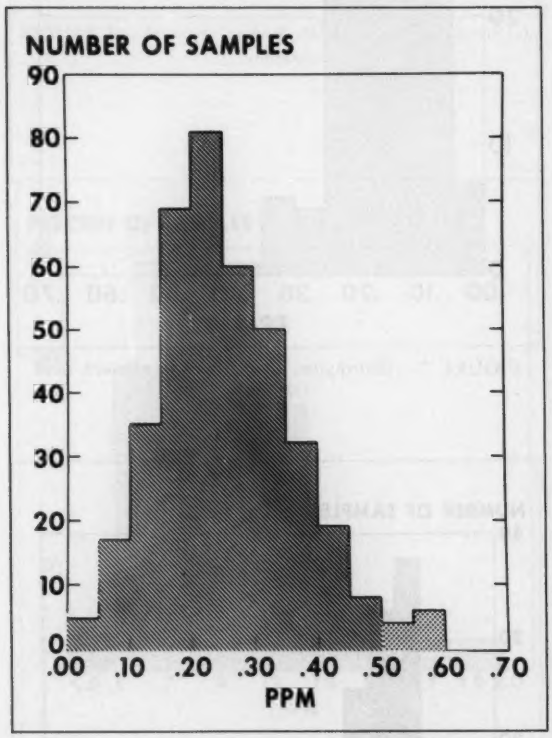

FIGURE 6.—*Distribution of mercury in albacore (NCA data)*

Since 1967 the Bureau of Sport Fisheries and Wildlife, U.S. Department of the Interior, has conducted a monitoring program for pesticides in fish collected from various lakes and streams throughout the United States. Results from an extensive survey for mercury in freshwater fish, recently reported by Henderson, Inglis, and Johnson (*16*), indicated that in 1969 values ranged from <0.05 to 1.25 ppm and in 1970 from <0.05 to 1.80 ppm total mercury in the edible portions. Of 100 monitoring stations, average values for total mercury exceeded the FDA guideline of 0.5 ppm at three stations in 1969 and at six stations in 1970.

Along with other collaborating organizations monitoring mercury pollution in freshwater areas of the United States, the Water Quality Control Branch (WQCB) of the Tennessee Valley Authority (TVA) has been cooperating with the Food and Drug Administration and the U.S. Environmental Protection Agency (EPA). In a recent report covering their survey of mercury in fish from TVA reservoirs (*17*), WQCB found significantly high levels of mercury in fish obtained from both the Pickwick, Tennessee, and the Kentucky reservoirs (Fig. 4, 5). After eliminating the discharge of mercury into these waters, TVA researchers have observed a downward trend in mercury concentrations among reservoir fish, though the level remains above 0.5 ppm. As overlaying mercury-free sediments continue to collect in these waters, researchers expect this downward trend to continue.

CANNED TUNA FISH

Analyses of over 3,000 samples of canned tuna (Table 5) show an average overall mercury content of about 0.25 ppm, with less than 4% over the 0.5 ppm guideline. The coefficient of correlation between weight of fish and mercury level is given for each type of fish and for all types combined for the National Canners Association (NCA) data. Weights were not available for the imported samples, and such correlations could not be examined. This correlation is highly significant in domestic samples for albacore ($p<0.001$), yellow fin ($p<0.001$), the "other" category ($p<0.01$), and all types combined ($p<0.0001$), indicating that the mercury concentration increases with an increase in fish size. The correlation for skipjack was not significant, perhaps because the largest weight for the skipjack was 25 lb, and the increased opportunity of the larger fish to concentrate the mercury may be more manifest in fish larger than 25 lb. Figures 6 and 7 show that the mercury concentration in albacore and skipjack tuna approaches a normal distribution; the larger albacore has the greater number of samples with elevated levels of mercury. Only in imported tuna (Fig. 8) is the distribution skewed above 0.5 ppm. More recent results illustrated in Figure 9, however, suggest a downward trend for both domestic packs and imported tuna. This probably indicates closer scrutiny by the suppliers, rather than any real reduction of mercury concentration in these fish species.

HALIBUT

During the 1971-72 mercury survey, FDA analyzed more than 500 samples of domestic and imported halibut (Table 6.) The overall average concentration of mercury was about 0.25 ppm, and about 13% of the samples were above the 0.5 ppm guideline.

SWORDFISH

Results for swordfish are quite different from those for halibut. Of 853 samples analyzed in 1971 (Table 7), over 95% exceeded the 0.5 ppm guideline and over 50% of the samples exceeded 1 ppm mercury. As Figure 10 shows, however, the concentration approaches a normal distribution, as in tuna, with the greatest number in the range 0.75-0.99 ppm. As a result of these findings, FDA recommended that the public not eat swordfish and that this commodity be recalled from the domestic market (*1*). Commercial swordfish usually average about 150 lb each; hence these findings are not surprising in view of the correlations with weight in tuna, as mentioned earlier.

COMMERCIAL FISH AND SEAFOOD

Among the more than 1,300 samples of 19 different types of other commercial fish and seafood collected in 1971, only six types included one or more fish with a mercury content above the 0.5 ppm guideline (Table 8). Of those species containing a significant number of samples, bonita and snapper averaged more than 0.2 ppm mercury. Although a few crab, cod, flounder, lobster, and herring reached this level, the high-level samples constituted less than 10% within each type.

SURVEY OF MERCURY IN FOOD (*5*)

Of all food examined for mercury content, measurable quantities were found only in shrimp when examined by the neutron activation technique (*12*); it had a high value of 0.043 ppm and a median value of 0.014 ppm (Table 9). Nonfat dry milk was next highest with a high of 0.027 ppm and a median of 0.010 ppm. The mercury level in nonfat dry milk, when reconstituted, is of the same order as that in fluid whole milk: approximately 0.002 ppm. All commodities except shrimp were also analyzed by the dithizone and the atomic absorption methods, which were not sensitive enough to measure with absolute precision such low levels of mercury. Table 9 gives the median and range of values in the 10 commodities found by the neutron activation method only.

TOTAL DIET SURVEYS

Results from the most recent total diet survey by the current neutron activation analysis method (*12*) are presented in Table 10 with results reported previously (*2*). All commodities except meat, fish, and poultry (Group II) contained less than 0.014 ppm mercury. The meat, fish, and poultry group contained mercury ranging from 0.004 to 0.041 ppm, depending upon the mercury level in the fish component. The amount of mercury currently found in red meat muscle tissue is about 0.010 ppm (1972, A. J. Spaulding, United States Department of Agriculture, *personal communication.*), comparable to the levels generally found in Fraction II.

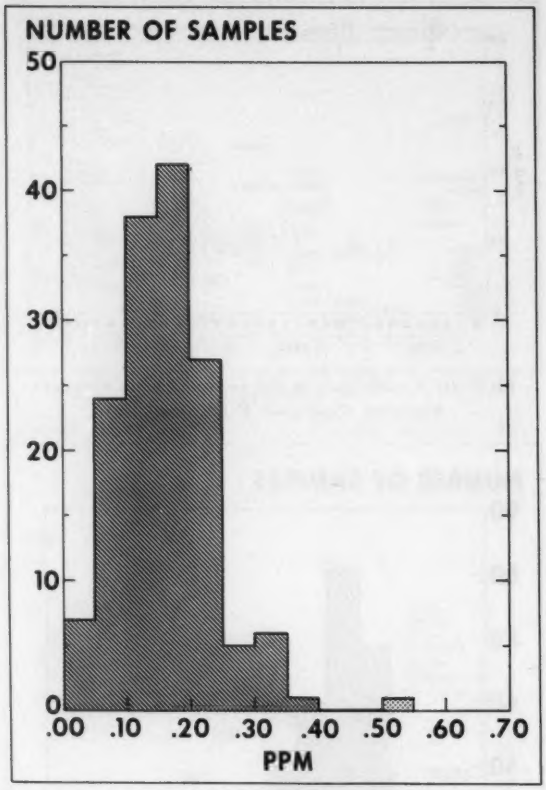

FIGURE 7.—*Distribution of mercury in skipjack tuna (NCA)*

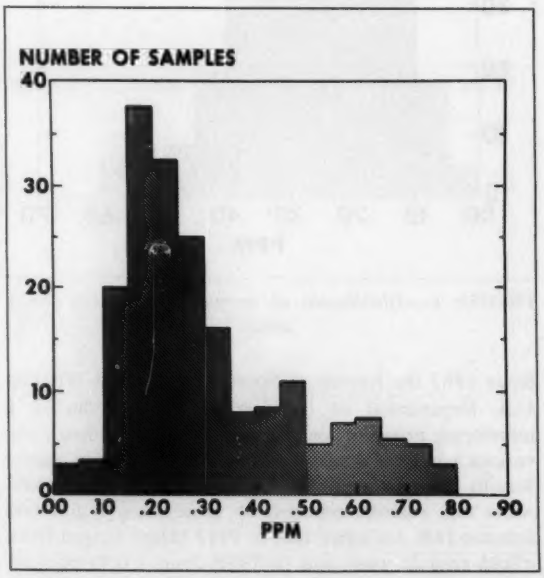

FIGURE 8.—*Distribution of mercury in imported tuna*

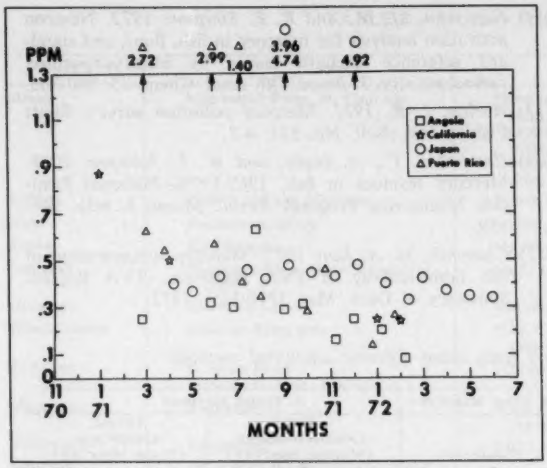

FIGURE 9.—*Mercury in both domestic and imported tuna combined*

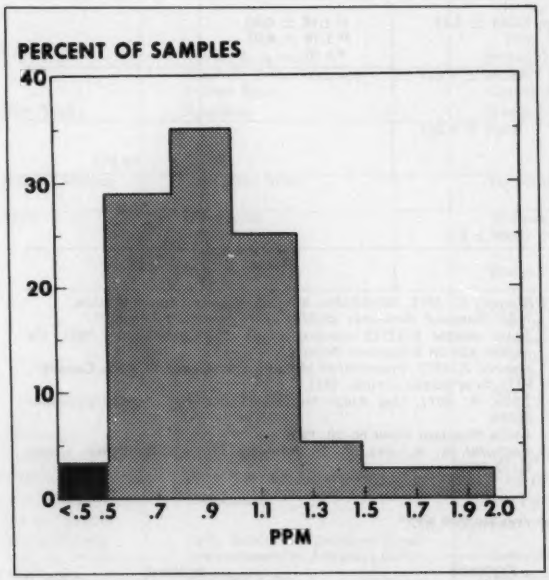

FIGURE 10.—*Distribution of mercury in swordfish*

The earlier results are higher than current data by one order of magnitude (*2*). This was probably due to the presence of low-level mercury contamination introduced in earlier sample preparation, the significance of which has been recognized only recently (*12*). This same factor also may have been responsible for the high results reported earlier in the Jervis study (*4*).

Conclusion

Of all commodities analyzed for mercury in the surveys reported in this paper, fish appears to present the only potential hazard to man. However, levels of mercury that exceed the 0.5 ppm guideline for fish are found only in the larger species (large tuna, halibut, and swordfish) of the commercially important varieties and in fish obtained from waters of known mercury pollution. In all other commodities, mercury either is not detectable or is present at levels approximating two orders of magnitude lower than the guideline for fish.

Acknowledgments

1. Data from the fish and foods survey were collated by the Office of Compliance, U.S. DHEW-FDA, with special cooperation of Mary J. Dolan. The FDA District inspectors and laboratory personnel (Fig. 1) who collected and analyzed the samples were responsible for the success of these surveys.

2. James Winbush, Janet Springer, and other members of the mathematical staff have assisted greatly in statistically evaluating data. Fish data were processed by Daryl C. Fleming of the Systems Analysis Branch, Office of Executive Director of Regional Operations.

3. The neutron activation analysis results of the foods survey were acquired through the efforts of James T. Tanner and colleagues (*12*) in the FDA facilities at the National Bureau of Standards reactor in Gaithersburg, Maryland. These facilities are made available to FDA through an interagency agreement among several agencies: DHEW-FDA and Department of Commerce NBS.

4. We appreciate the cooperation of other organizations mentioned in the text, who permitted their data to complete results of the study.

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(17) *Churchill, M. A. June 1972.* Mercury concentration in fish flesh—survey of TVA reservoirs. TVA Report, Summary of Data, May 1970-May 1972.

TABLE 1.—*Comparative results (ppm) of mercury tests, using different analytical methods*

Commodity	Radiochemistry of Neutron Activated Samples for Total Mercury [1]			Other Methods	
	Sulfide Precipitation	Electrolytic Deposition	Pyrolysis [2]	Gas Chromatography (Methyl Mercury)	Atomic Absorption (Total Mercury)
FDA shrimp	0.033 ± 0.003 0.029 ± 0.003 0.026 ± 0.003 0.043 ± 0.004			[3] 0.03 0.03 0.04 0.06	[4] 0.03 0.02 0.00 0.01
Swedish pike [5] F-410-28	2.16 ± 0.22	2.24 ± 0.22 [6] 1.94	2.20 ± 0.15	[3a] 2.19 ± 0.10 [3b] 2.22 ± 0.03 [6] 1.88	
Swedish pike F-410-30	1.29 ± 0.13	1.17 ± 0.11 [6] 1.10	1.18 ± 0.15	[3a] 1.18 ± 0.02 [3b] 1.10 ± 0.03 [6] 1.10	
Orchard leaves [7]	0.148 ± 0.01	0.162 ± 0.02 0.154 ± 0.02 0.169 ± 0.02	0.155 ± 0.015		
CHPB flour [8]	0.011 ± 0.01 [9] 0.014 ± 0.004	0.012 ± 0.002 0.015 ± 0.002 0.008 ± 0.002	0.011 ± 0.003		[8] 0.013
FDA flour [10]	0.002 ± 0.002 [11] 0.004				
IAEA flour [12]	4.6 ± 0.5 4.9 ± 0.3		4.87 ± 0.5		
Bowman kale [13]	0.25 ± 0.03 [12] 0.23				

[1] All FDA neutron activation analysis data represent single determinations; therefore, ± deviations represent counting error and radiochemical uncertainties arbitrarily set at ± 10%

[2] *Rook, H. L., T. E. Gills, and P. D. Lafleur. 1972.* Anal. Chem. 44: 1114.

[3] *L. R. Kamps. 1971.* FDA Headquarters. Private communication. (a) Samples analyzed on a wet basis, average of 3 replicates; (b) samples analyzed after freeze drying, average of duplicates.

[4] *FDA District results. 1971.* Office of Compliance Report.

[5] Pike samples courtesy of National Institute of Public Health, Stockholm, Sweden.

[6] *Westoo, G. 1971.* Stockholm, Sweden. Private communication.

[7] *NBS Standard Reference #1571. 1971.* "Orchard Leaves."

[8] Flour sample C-32572 courtesy of H. M. Cunningham. 1971. Canadian Health Protection Branch.

[9] *Somers, E. 1971.* Proceedings Mercury Conference, Ottawa, Canada.

[10] FDA flour survey sample. 1971.

[11] *Lyon, W. 1971.* Oak Ridge National Laboratory. Private communication.

[12] IAEA Standard Flour 66/10. 1969.

[13] *Nadkarni, R. A., and W. D. Ehmann. 1969.* J. Radioanal. Chem. 3:175-185.

TABLE 2.—*Mercury in freshwater fish*[1]

State	Areas	Findings	Actions
Alabama	Pickwick Reservoir, tributaries of Tennessee River, Tombigbee River	Trace to 0.5 ppm	Closed to commercial fishing
Arizona		No findings reported	
California	Sacramento-San Joaquin Delta Clear Lake	Up to 1.27 ppm	No closures
Colorado	Eastern irrigation reservoir	0.04 to 0.08 ppm	No closures
Connecticut		No findings reported	
Delaware	Delaware River, Delaware Bay	<0.5 ppm	No closures
Florida	Pulp mill areas	No Hg found [2]	—
Georgia	Fresh and estuary waters	Not reported	Savannah River and Brunswick Estuary closed
Hawaii		No findings reported	
Idaho		No findings reported	

TABLE 2.—*Mercury in freshwater fish*[1]—Continued

STATE	AREAS	FINDINGS	ACTIONS
Illinois	Mississippi River, St. Clair Co.	Three samplings each: carp, 0.09-15 ppm catfish, 0.44 ppm white bass, 0.20 ppm perch, 0.15 ppm shad, 0.08 ppm	No closures
Indiana	Waters of Lake Michigan	Whole fish, 0.18 ppm [2]	No closures
Iowa	Random sampling	0-0.002 ppm [2]	No closures
Kansas	Kaw Rivers	Hg found [2]	No closures
Kentucky	Tennessee River below Kentucky Dam	0.6 to 1.14 ppm	Stopped commercial fishing in Tennessee River area of Kentucky
Louisiana	Calcasieu Lake	Not reported	Warning against eating lake fish
Massachusetts	Launton River area	Fish, 0.17-1.21 ppm; shellfish, mussels, clam, 0.3-4 ppm	No closures
Michigan	St. Clair River Wyandotte, Detroit River	0-7 ppm [2]	Commercial closure of St. Clair River, Lake St. Clair, Lake Erie
Minnesota	Statewide	<0.5 ppm except Red River of the North	No closures
Mississippi	Unspecified	0.05-1.14 ppm (in Alabama)	No closures
Missouri	No known Hg pollution sources [2]		
Montana	Above and below pulp mill	Trace [2]	No closures
Nebraska		No findings reported	
Nevada		No findings reported	
New Hampshire	Connecticut River Merrimack River	Of fish analyzed, ½ >0.5 ppm; ¼ >0.5 ppm; highest, 1.3 ppm	No closures
New Jersey	Arthur Kill River	0.03-0.21 ppm	No closures
New Mexico	Navajo Lake	All varieties, 0-0.16 ppm; brown trout, 1.14-1.16 ppm; bullheads, 0.68 ppm; catfish & trout, 0.34 ppm; bluegills, 0.4 ppm	
	Avalon Reservoir	0.05-0.22 ppm	Warning against eating fish
	Elephant Butte Reservoir	0.14-0.7 ppm	
	Animas River	Catfish & trout, 0.13 ppm	
New York	Statewide	Range 0.01-8.2 ppm	Warning against eating fish; Lake Ontario; Lake Champlain; Lake Erie; St. Lawrence, Oswego & Niagara Rivers
North Carolina	Cape Fear River	Hg contamination found [2]	No closures but monitoring of inland areas initiated
Ohio	Kiser Lake	Walleye, 0.55 ppm	
	Buckeye Lake	White bass, 0.59 ppm	
	Maumee River		
	Lake Erie	Range 0.04-1.51 ppm	Lake Erie closed to commercial fishing; warning to others
	Western Basin	Coho, 0.24 ppm; walleye, 0.62-1.4; white bass, 0.8 ppm; perch, 0.48-0.78 ppm; carp, 0.67 ppm; mullet, 0.47 ppm; drum, 0.29-0.65 ppm; catfish, 0.07-4.6 ppm	
	Vermilion area	Perch, 0.22 ppm; carp, 0.22 ppm	
	Cleveland area	Perch, 0.55 ppm; mullet, 0.5 ppm	
Oklahoma		No findings reported	
Oregon	Unspecified	No Hg found	
Pennsylvania	Lake Erie only Hg source	0.5-3 ppm	Warning against Lake Erie fish
Rhode Island	Unspecified	No Hg found	
South Carolina	No findings reported		Savannah River closed Augusta to Coast
South Dakota	Oahe Reservoir, Cheyenne River Impoundment to Missouri River	0.03-0.35 ppm	No closures
Tennessee	Pickwick Lake	No data cited	Closed to commercial fishing
Texas	Houston Ship Channel	Waters, 19 ppm (?)	Lavaca Bay closed
	Lavaca Bay	oysters >5 ppm	
Utah	Limited survey	0.03-0.06 ppm	No closures
Vermont	Lake Champlain	⅓ of fish samples >0.5 ppm	
	Other lakes and ponds	⅛ >0.5 ppm	Closed to commercial fishing
Virginia	No findings reported		Warning against fish from N. Fork Holston River
Washington	Unspecified	Unspecified	No waters closed in any areas
West Virginia	Ohio and Monongahela Rivers	No data	Closure of these reservoirs
Wisconsin	Wisconsin River of known Hg use	High as 4.62 ppm	Restraint warning
Wyoming	Ocean Lake Reservoir; Alcova Reservoir	0.05-0.116 ppm	No closures

[1] Survey initiated by USDI—Federal Water Quality Administration (FWQA), 1970.
[2] Reported by R. H. Stroud. *1971.* Marine Sport Fisheries Research. Sport Fishing Inst. Bull. No. 221 (*15*).

TABLE 3.—*Mercury in Great Lakes fish, 1970*

Region	Type	No. of Samples	Mean ± standard deviation (ppm)	Percent in ppm ranges of:				
				<0.1	0.1-0.50	0.51-1	>1	>2
Lake Erie	Walleye	26	0.58 ± 0.26	4	27	61	8	2
	Perch	53	0.24 ± 0.14	8	85	7	0	—
	White bass	37	0.49 ± 0.31	6	38	48	8	0
	Sheepshead	29	0.28 ± 0.21	15	65	20	0	—
	Carp	19	0.28 ± 0.29	17	75	4	4	0
	Mullet	11	0.21 ± 0.16	27	73	0	0	—
	Sucker	14	0.21 ± 0.13	21	79	0	0	—
	Catfish	20	0.23 ± 0.20	30	55	15	0	—
	Smallmouth bass	13	0.51 ± 0.19	0	69	31	0	—
	All others	55	0.19 ± 0.23	44	49	7	0	—
Lake St. Clair	Perch	18	0.88 ± 0.75	0	40	30	30	2
(Ontario Province, Canada)	All others	32	0.48 ± 0.32	3	56	34	7	0
Lake Michigan	All types	40	0.11 ± 0.11	62	38	0	0	—
Lake Ontario	All types	74	0.30 ± 0.30	12	74	10	4	0
Lake Huron	All types	23	0.19 ± 0.11	22	78	0	0	—
Lake Superior	All types	10	0.13 ± 0.11	20	80	0	0	—
Columbia River [1]	All types	27	0.05 ± 0.07	63	37	0	0	—
Puget Sound [1]	All types	11	0.03 ± 0.07	82	18	0	0	—

[1] These samples were collected from assumed uncontaminated Western areas for comparison with Great Lakes fish.

TABLE 4.—*Mercury in fish from various freshwater areas, 1970*

Region	Type of Fish	Number of Samples [1]	Mean ± standard deviation (ppm)	Percent in ppm ranges of:				
				<0.1	0.1-0.50	0.51-1	>1	>2
Savannah River, Augusta, Ga.	All types	12	0.56 ± 0.26	11	32	57	0	—
Beaverhead River, Mont.	All types	10	0.57 ± 0.34	0	60	30	10	0
Belle Pourche, R.I.	All types	12	0.22 ± 0.22	42	50	8	0	—
Calcasieu Lake, La.	All types	16	0.39 ± 0.41	31	31	31	7	0
Cape Fear River, N.C.	Catfish	9	1.14 ± 0.59	0	12	33	55	0
Cherokee, Tenn., and Boone, Ky., Reservoir	All types	13	0.15 ± 0.14	46	54	0	0	—
Chocooloco Creek	All types	8	0.39 ± 0.16	0	75	25	0	—
Lake Charles, La.	All types	23	0.31 ± 0.35	22	65	9	4	0
Mississippi River	All types	54	0.22 ± 0.28	37	48	9	6	0
Muscle Shoals, Ala.	All types	6	0.97 ± 0.75	0	34	33	33	1
Niagara River	All types	8	0.15 ± 0.07	1	99	0	0	—
Oake Reservoir, Dakotas	All types	12	0.29 ± 0.24	0	84	16	0	—
Riegelwood, N.C.	Catfish	14	0.84 ± 0.27	0	8	71	21	0
	Others	12	1.03 ± 0.56	0	8	42	50	0
Red River, Texas	All types	10	0.17 ± 0.09	20	80	0	0	—
Sheffield, Ala.	All types	8	1.00 ± 0.89	0	38	12	50	2
St. Lawrence River	All types	9	1.16 ± 0.50	0	12	44	44	1
Tennessee River	All types	11	0.20 ± 0.12	18	82	0	0	—
Wheeler Lake, Ala.	All types	7	0.29 ± 0.09	0	100	0	0	—
Whitlock Bay	All types	7	0.13 ± 0.05	27	73	0	0	—
Yellowstone and Tonque Reservoirs, Mont.	All types	10	0.16 ± 0.08	40	60	0	0	—
Nine other areas [2]	All types	29	0.06 ± 0.03	86	18	0	0	—

[1] The atomic absorption method was used to analyze samples from all but three sources: Calcasieu Lake, Lake Charles, and the Mississippi River.

[2] Each body of water had 3-5 samples.

TABLE 5.—*Mercury in tuna fish*

	Skipjack	Albacore	Yellowfin	Other
IMPORTED SAMPLES PROCESSED BY FDA				
Number in sample	936	1437	135	200
Mean mercury level (ppm)	0.20	0.31	0.17	0.31
Standard deviation	0.085	0.11	0.097	0.18
Upper 99% confidence limit on mean	0.21	0.314	0.19	0.34
Upper 99% tolerance limit on 99% of population	0.41	0.59	0.44	0.80
Upper 99% tolerance limit on 95% of population	0.35	0.51	0.36	0.67
DOMESTIC SAMPLES PROCESSED BY NATIONAL CANNERS ASSOCIATION				
Number in sample	149	383	288	70
Mean mercury level (ppm)	0.16	0.25	0.21	0.20
Standard deviation	0.078	0.10	0.12	0.12
Upper 99% confidence limit on mean	0.17	0.26	0.23	0.24
Upper 99% tolerance limit on 99% of population	0.37	0.52	0.51	0.55
Upper 99% tolerance limit on 95% of population	0.31	0.44	0.42	0.46
Mean weight [1]	8.18	31.17	50.60	24.86
Correlation coefficient [1]	0.041	[2] 0.33	[2] 0.33	[3] 0.44, [2] 0.67

[1] Based on fewer samples than given above.
[2] Significant at $P<0.001$.
[3] Significant at $P<0.01$.

TABLE 6.—*Mercury concentration in halibut*[1]

State and County, or Country	Collection Month & Year		No. of Samples	Mercury, ppm High	Low	Average	± σ	No. of Samples >0.5 ppm	Percent of Samples >0.5 ppm
Alaska, Prince of Wales Co.	8, 10, & 11	71	60	0.92	0.12	0.39	0.19	13	20
California, Alameda Co.	2	71	3	0.16	0.04	0.10			
Los Angeles Co.	2 & 9	71	6	0.37	0.07	0.20			
Illinois, Cook Co.	2 & 3	71	8	0.71	0.05	0.19	0.25	1	
Massachusetts, Suffolk Co.	2	71	4	1.40	0.08	0.41		1	
Oregon, Clatsop Co.	9	71	13	0.41	0.18	0.28	0.08		
Pennsylvania, Phila.	2	71	17	0.29	0.03	0.14	0.07		
Washington, King Co.	7	71	9	0.31	0.07	0.13	0.08		
	8	71	78	0.76	0.08	0.29	0.13	3	4
	9	71	65	1.52	0.13	0.45	0.27	20	30
	10	71	64	1.50	0.07	0.40	0.34	17	27
	11	71	5	0.28	0.07	0.21	0.09		
	5	72	5	0.73	0.60	0.70	0.06	5	100
Washington, Snohomish Co.	10	71	12	0.49	0.11	0.18	0.10		
	11	71	6	0.29	0.18	0.24	0.05		
Washington, Whatcom Co.[2]	8	71	23	0.12	0.06	0.12	0.06		
	10	71	27	0.59	0.07	0.23	0.13	3	11
Canada [3]	7	71	5	0.39	0.05	0.24	0.15		
	8	71	6	0.13	0.05	0.11	0.06		
	9	71	17	0.46	0.06	0.16	0.10		
	10	71	22	0.26	0.02	0.17	0.07		
	11	71	15	0.74	0.10	0.29	0.21	3	23
	12	71	12	1.10	0.04	0.30	0.28	2	17
	1	72	11	0.49	0.16	0.37	0.11		
	2	72	11	0.49	0.10	0.22	0.14		
	3	72	3	0.30	0.17	0.22	0.07		
	5	72	6	0.49	0.18	0.28	0.14		
	6	72	4	0.25	0.03	0.15	0.09		
Japan	10	71	3	0.31	0.08	0.22	0.12		
	11	71	3	0.42	0.24	0.30	0.1		
	3	72	6	0.32	0.03	0.21	0.09		
	5	72	7	0.25	0.12	0.16	0.05		
	6	72	4	0.12	0.10				

[1] Overall total = 543 samples with an overall mercury concentration = 0.25 ppm with 68 (13%) in excess of 0.5 ppm.
[2] Total sample for Washington State = 294; total >0.5 ppm = 48 (16%).
[3] Total Canadian sample = 122; total >0.5 ppm = 5 (4%).

TABLE 7.—*Distribution of mercury levels in swordfish above 0.5-ppm guideline*[1]

Range of Mercury Levels, ppm	Percent of samples at this level
<0.50	—
>0.50-0.74	13.7
0.75-0.99	33.2
1.00-1.24	26.5
1.25-1.49	15.3
1.50-1.99	8.5
2.00-2.99	2.4
3.00->3.00	0.3
	99.9

[1] Of all swordfish sampled, 95% exceeded 0.5 ppm mercury.

TABLE 8.—*Mercury in wholesale fish*

Fish Type	Mean Mercury Level, ppm	Total Sub-samples	No. of Lots	Std. Dev. Within Lots	Std. Dev. Between Lots (Component of Variance)	Upper 99% Confidence Limit on Mean	Upper 95% Tolerance Limit on 99% of Lots	Upper 99% Tolerance Limit on 99% of Lots
Bonita	0.30	41	34	0.04	0.19	0.38	0.87	0.94
Clams	0.03	158	81	0.03	0.03	0.04	0.13	0.13
Cod	0.09	170	80	0.04	0.07	0.11	0.31	0.32
Crab	0.11	236	85	0.09	0.09	0.14	0.39	0.41
Flounder	0.08	156	76	0.03	0.05	0.09	0.23	0.24
Halibut	0.14	151	82	0.03	0.07	0.16	0.38	0.40
Haddock	0.04	179	77	0.01	0.03	0.05	0.13	0.13
Herring	0.07	107	77	0.01	0.05	0.08	0.20	0.21
Lobster	0.07	185	83	0.02	0.06	0.09	0.23	0.24
Mackerel	0.12	140	91	0.11	0.20	0.17	0.70	0.74
Oysters	0.03	203	86	0.02	0.04	0.04	0.15	0.18
Perch	0.06	209	83	0.02	0.06	0.07	0.22	0.23
Salmon	0.04	99	78	0.03	0.02	0.05	0.13	0.14
Sardines	0.02	104	76	0.01	0.02	0.03	0.08	0.08
Scallops	0.02	171	76	0.01	0.02	0.03	0.07	0.08
Snapper	0.31	186	86	0.10	0.15	0.35	0.75	0.78
Trout	0.09	151	83	0.03	0.10	0.12	0.37	0.39
Whitefish	0.05	65	48	0.03	0.03	0.07	0.18	0.19
Whiting	0.06	133	61	0.06	0.04	0.08	0.22	0.23

TABLE 9.—*Neutron activation analysis for mercury in foods (12)*

Commodity	No. of Samples	Mercury Residues in ppm [2]	
		Median	Range
(1) Flour	28	<0.003	<0.003-0.006
(2) Nonfat dry milk	3	0.010	<0.004-0.027
(3) Sugar	22	<0.003	<0.003-0.010
(4) Potatoes	33	0.003	0.001-0.015
(5) Raw ground beef	23	0.003	<0.002-0.007
(6) Chicken breast (raw and boned)	24	0.003	<0.001-0.007
(7) Shrimp	32	0.014	0.005-0.043
(8) Beef liver	22	0.003	<0.002-0.008
(9) Eggs	33	<0.002	<0.002-0.005
(10) Fluid whole milk	32	<0.001	<0.001-0.009

[1] With the exception of (1), (2), and (3), all commodities were freeze dried, but result were calculated on a wet-weight basis using the moisture content for each sample.
[2] Upper limits represent twice the standard deviation of the background count.

TABLE 10.—*Neutron activation analysis for mercury in total diets*

Commodity Groups [2]	Mercury Concentration (ppm)[1]				
	Southern Region [3] (Baltimore)	Northeast Region (Boston)	Central Region (Kansas City)	Central Region (Minneapolis)	Western Region (Los Angeles)
I Dairy Products	<0.001	<0.001	<0.001	0.003	0.002
II Meat, Fish, and Poultry	0.030	0.013 0.026 0.041	0.006 0.004 0.013	0.009	0.027
III Grain and Cereal Products	0.003	0.012 0.004	0.005	<0.002	<0.002
IV Potatoes	0.003	0.002 0.013	<0.002	0.003	<0.001
V Leafy Vegetables	0.001 0.009	0.003 0.006	0.004 0.002	<0.001	<0.001
VI Legume Vegetables	<0.002	<0.001	<0.002	<0.001	<0.001
VII Root Vegetables	0.002	<0.001	<0.001	<0.001	<0.001
VIII Garden Fruits	0.002	0.002	<0.001	<0.001	<0.001
IX Fruits	<0.002	0.002	0.003 0.002	<0.001	<0.001

[1] All values listed are results of single determinations. Therefore the uncertainty of the data due to counting error and radiochemistry is approximately ± 10%. The data were acquired by J. T. Tanner and M. H. Friedman of this laboratory. "Upper limits" represent twice the standard deviation of the background count.
[2] Oils (X), Sugar-adjunct (XI) and Beverages (XII) are not readily freeze dried; therefore they are not suitable for neutron activation analysis at this time.
[3] USDA (9) regions.

Levels of Mirex and Some Other Organochlorine Residues in Seafood from Atlantic and Gulf Coastal States

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ABSTRACT

A seafood monitoring program for the insecticide mirex was set up in 1971. Seventy-seven composite samples of oysters, crabs, shrimp, fish, and fish products were collected from seven locations within the area where mirex is used and from two check locations outside the treatment areas. The study showed that mirex occurred in only nine of the 77 samples (0.005-0.024 ppm range), all from near Savannah, Georgia. DDT or its metabolites occurred in 74 samples (0.002-2.475 ppm range). The polychlorinated byphenyl (PCB) Aroclor 1260 occurred in 46 samples; if extensive new methods of cleanup had not been used, these PCB residues probably would have been interpreted as mirex. Several early studies reporting extensive residues of mirex in marine life were made before the possibility of confusing Aroclor 1260 with mirex had been realized; hence these earlier studies may be in error.

Introduction

Throughout a nine-State region in the Southeastern United States, baits containing the insecticide mirex are the main method of controlling the imported fire ant, an important agricultural pest and a nuisance to humans. At least 95% of the mirex used in the United States as an insecticide is used to control this one pest; since 1967 more than 10 million acres a year have been treated with mirex (*1*). Since many of the areas with the heaviest infestation of the imported fire ant are in coastal regions, a considerable amount of the mirex used has been near the coastline of the Atlantic Ocean and the Gulf of Mexico.

Mirex is an organochlorine pesticide and like most other organochlorine pesticides has a long field life. When applied at the normal rate, 1.7 g actual toxicant per acre, minute residues have been found in a wide variety of nontarget organisms in the treated areas (*1*).

In 1968 and 1969 the U.S. Department of Agriculture (USDA) conducted a study on Cat Island off the coast of Mississippi, and in 1969 and 1970 USDA cooperated with the U.S. Department of the Interior (USDI) at Charleston, S.C., in a similar study. The studies, both unpublished, showed residues ranging from a high of 2 ppm in some bottom-feeding fish immediately following a treatment (probably indicating that the fish had fed directly on the bait) to a low of 0.001 ppm. Small residues could be detected as much as 2 years later. These two studies were restricted to small bays or estuaries where mirex was applied directly to the water or to the immediately surrounding salt marsh. The USDA has not sampled fish and marine life from areas lying off treated sections of the coastline.

Other studies have indicated that mirex residues were being found well outside the immediate treatment area and were showing up in commercial catches of marine life destined for human consumption. Butler (*2*) reported mirex as one of the most abundant of the organochlorine pesticides found in shellfish off the Atlantic, Gulf, and Pacific coasts. In a survey of pesticides in blue crabs off the coast of South Carolina (*3*), North Carolina, Georgia, and Florida (*4*), 35% of the samples from the 20 collecting sites contained mirex residues with a mean of 0.076 ppm and extremes of 0.005 to 0.389 ppm. No similar monitoring for mirex has been conducted with marine fish, but the widespread occurrence of mirex in invertebrates indicates that larger predators of the same area could have higher residues of this pesticide.

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The occurrence of even small residues of mirex in crustaceans has taken on new significance with the discovery that mirex, like many other organochlorine pesticides, is lethal to juvenile shrimp, crabs (*5*), and juvenile crayfish (*6*).

The USDA, as part of an overall study of the distribution of mirex through the environment, initiated a preliminary survey for mirex in seafood in spring 1971. Results of this study are the subject of this report. Primary purpose of the study was to survey various types of seafood and marine products to determine how extensively mirex residues were occurring.

Sampling Procedures

The seafood analyzed in this study was collected from nine sampling areas shown in Figure 1. The areas were not chosen randomly. To assure finding residues for this preliminary study, researchers collected some samples from areas where mirex had been used extensively. Correspondingly, the first seven of the following sampling areas were set up in areas with a documented history of mirex use; sampling areas 8 and 9 were located outside mirex treatment areas. The following paragraphs describe specific areas.

(1) *Mississippi Sound:* This region lies between the Mississippi River Delta and the coast of Mississippi. It is fed by several rivers, the most notable of which is the Pearl River, and the drainage from Lake Pontchartrain in Louisiana. All the rivers drain areas which are heavily infested with the imported fire ant and which have been treated extensively with mirex. The coast of Harrison County was treated aerially in 1966 and 1969, and much of Hancock County was treated in 1969 and 1970; Cat and Ship Islands in Mississippi Sound received three applications of mirex in 1968 and 1969 in an experimental eradication trial.

FIGURE 1.—*Mirex sampling areas, Atlantic and Gulf Coast States, 1971. Numbers 1 to 9 show sampling sites, shaded areas indicate heaviest use of mirex. Dotted line denotes approximate range of imported fire ant.*

(2) *Mobile Bay:* Mobile Bay, Alabama, has not been the site of any organized control programs. However, individual farmers have attempted to control the imported fire ant in the surrounding areas in one of the largest mirex programs in the Southeast. Most farmers in the area mix mirex bait with fertilizer which they apply to pastures every spring.

(3) *Tampa Bay:* Approximately 3 million acres surrounding Tampa Bay, Florida, including the counties of Pinellas, Hillsboro, Polk, Hardee, Sarasota, and Manatee, received two or three aerial applications of mirex from 1967 to 1969 as part of a Federal - State cooperative program. Since 1969 the headwaters of many of the rivers feeding this bay also drained areas where State - farmer control programs have been effective. Probably the second largest amount of mirex ever to be applied areas within the range of the imported fire ant.

(4) *Jacksonville, Florida:* Samples were collected from the mouth of St. John's River. Ants have never been too extensive in the area, but several control programs have been conducted in the past 5 years. It probably has received less mirex than any of the other six sampling areas within the range of the imported fire ant.

(5) *Savannah, Georgia:* Approximately 2.5 million acres of land in the area of Savannah, Georgia, and adjacent South Carolina received three complete blanket applications of mirex bait between the fall of 1967 and 1969. This was an experimental attempt to eradicate an isolated pocket of ants, and was followed in 1970 by smaller programs farther inland. The program included extensive treatment of the marsh areas along the coasts of South Carolina and Georgia. To date, this is probably the largest area of marsh, tidal flat, and open water which has been treated in the Southeast, and the total amount of mirex used since 1968 is probably the largest ever used in the United States. Residues of mirex from marine life in this area have been detected in routine monitoring conducted along with the eradication experiment.

(6) *Charleston, South Carolina:* A block of approximately 500,000 acres was treated in the Charleston area in the fall of 1969-70. The area treated stretched from Berkeley County through Dorchester, Charleston, and Coleton Counties. Most areas were treated at least twice.

However, the coastal area, a strip 3 to 12 miles wide between the treatment block and the coast, was not treated, in compliance with USDA policy on the use of mirex (*7*). The headwaters of numerous streams that drained treated areas did empty into the coastal strip, however, which included all coastal islands and beaches, tidal marshes, and major estuaries.

(7) *Morehead City, North Carolina:* A small isolated infestation of the imported fire ant near Morehead City in Carteret and Onslow Counties, North Carolina, is presently the point farthest north which is infested by this pest. Since 1963 parts of the area have been treated yearly to reduce the population of the ant.

(8) *Chesapeake Bay and* (9) *Delaware Bay:* These two sampling areas are located well beyond the present range of the imported fire ant and there is no reason to believe that mirex has been applied in either area. The two areas were chosen as check areas.

Field inspectors for the Animal and Plant Health Inspection Service, USDA, stationed in the nine areas, were assigned the task of collecting the necessary samples. Each inspector was furnished a list of desired samples and instructions for collecting, handling, and shipping them. Samples were usually purchased from commercial sources such as fishing boats, processing plants, or wholesale distribution points. Occasionally samples of game fish were obtained from sport fishermen. When possible, samples of the desired animals were obtained from three or more sources in each sampling area and combined to give a single composite sample. Types and sizes of samples obtained from each sampling area are given in Tables 1 and 2. Samples were wrapped in aluminum foil, frozen, and shipped to Gulfport, Mississippi, for analysis. At Gulfport they were rechecked and their identifications were verified. If the samples were too small or represented too few locations within a sampling area, inspectors were requested to furnish additional samples. Considerable effort was made to verify that the samples had come from the designated sampling area and had not been shipped or carried in from outside.

Analytical Procedures

Samples were thoroughly scrubbed to remove mud, algae, and other residues; they were ground whole and mixed in a Waring blender to make a composite sample. Samples were prepared and analyzed on a whole-body basis as received, except shellfish which were first shucked. Each sample of seafood usually consisted of a composite of five or more individuals, except the larger game fish. A 20-g subsample of the composite was removed and analyzed by our standard analytical method (*1*). Basically this consists of extracting with a mixture of hexane and isopropanol, and treating with concentrated sulfuric acid cleanup. The sulfuric acid destroys dieldrin, endrin, and organophosphorus insecticides, but the improvement in sensitivity by this cleanup was considered more than adequate compensation for the loss of these other pesticides. The final extract was cleaned up on a Florisil column and concentrated to the desired level for analysis. If polychlorinated biphenyls (PCB's) were suspected in the first analysis, their presence usually being indicated by a series of characteristic peaks, the sample was reprocessed to separate the PCB's from the pesticides. This technique is basically that described by Amour and Burke (*8*) but has been modified according to Gaul and Cruz-LaGrange (*9*) and our own laboratory (*1*).

After concentrating to the appropriate volume, the extraction from both methods of cleanup were chromatographed on a Hewlett-Packard Model 402 dual column gas chromatograph equipped with dual electron capture detection. Each sample was always analyzed on two different columns: the first column was a mixture of 1.5% OV-17 and 1.95% QF-1 on Gas Chrom Q. The temperatures of the injector, oven, and detector were 250°C, 200°C, and 210°C, respectively. The second column was 2% DC-200 Gas Chrom Q with injector, oven, and detector temperatures of 245°C, 175°C, and 205°C, respectively. Argon-methane at 80 ml/min was the carrier gas. Level of detection was 0.001 ppm for DDT and its metabolites, 0.005 ppm for mirex, and 0.01 ppm for the PCB, Aroclor 1260. Quantitative analysis for the PCB is still being developed, so the values presented should be considered tentative.

Results and Discussion

Table 2 presents the residue levels of mirex, DDT and its metabolites, and PCB Aroclor 1260 found in 77 seafood samples. DDT and its metabolites were recovered in 74 samples (range 0.002-2.475 ppm). The PCB Aroclor 1260 was found in 46 samples (range 0.01-1.17 ppm). Mirex was found in only 9 samples (range 0.007-0.024). All samples containing mirex were from around Savannah, Georgia, an area with a history of concentrated mirex use, among the most extensive in the United States. The recovery of mirex in only 12% of the samples, all from one area, could indicate that mirex is not so general nor widespread a contaminant of seafood as are PCB's and DDT. This does not correspond to earlier seafood studies (*2,3,4*) which reported that mirex occurred much more frequently and densely in many of these same collection sites.

Probably the reason for the discrepancy between this study and earlier studies is the confusion of Aroclor 1260 with mirex. The retention time for the last peaks of Aroclor 1260 is almost identical to the retention

time for mirex on most columns routinely used for analyzing mirex (*1*). Unless extensive additional cleanup procedures are employed, such as those used in this study, it is almost impossible to separate these two peaks. In this study, if the problem of PCB confusion had not been recognized and the special cleanup procedures used, the PCB peaks probably would have been reported as mirex. The possibility of confusing PCB's with the organochlorine pesticides was not generally recognized until 1970, and methods for distinguishing PCB's from mirex were not developed for general use until 1971. Since the three previous studies which reported mirex in seafood were all conducted before 1971, they probably did not recognize the problem and may have inadvertently reported the PCB Aroclor 1260 as mirex.

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TABLE 1.—*Summary of seafood samples from Atlantic and Gulf Coastal sites*

Location	Type of Seafood [1]							
	Crabs	Shrimps	Oysters & Shellfish	Squids	Predators/ Game Fish	Bottom Fish	Herring	Fish Products
1. Mississippi Sound	+	+	−	+	+	−	−	+
2. Mobile Bay	+	+	+	+	+	+	+	−
3. Tampa Bay	+	−	−	−	+	+	−	−
4. Jacksonville, Fla.	+	+	−	−	+	+	−	−
5. Savannah, Ga.	+	+	+	+	+	+	+	−
6. Charleston, S. C.	+	+	+	+	+	+	−	−
7. Morehead City, N. C.	+	+	+	−	+	+	−	+
8. Chesapeake Bay	+	−	−	−	+	−	+	−
9. Delaware Bay	+	−	−	−	+	+	−	−

[1] Plus sign (+) denotes sample collected minus sign (−) denotes no sample collected.

TABLE 2.—*Mirex, DDT and metabolites, and PCB residues in seafood*[1]

Species	Sample quantity	Residues in ppm					
		DDE	TDE	DDT	Total DDT & Metabolites	Aroclor 1260	Mirex
SAMPLING AREA 1—MISSISSIPPI SOUND							
Crabs	15	0.102	0.024	0.020	0.146	0.07	—
Shrimp	1 kg	0.004	—	0.003	0.007	—	—
Squid	1 kg	0.001	0.009	0.007	0.017	0.03	—
Flounder	3	0.031	0.007	0.009	0.047	0.03	—
Speckled sea trout	3	0.100	0.040	0.060	0.200	0.20	—
Spanish mackerel	3	0.095	0.026	0.040	0.161	0.06	—
Weak fish	5	0.049	0.010	0.050	0.109	0.12	—
Atlantic whiting	5	0.070	—	0.020	0.090	0.10	—
Fish oil	1 liter	0.070	0.030	0.020	0.120	0.02	—
Fish meal	1 kg	0.030	0.016	0.011	0.057	0.02	—
Ground fish (unprocessed)	1 kg	0.120	0.030	0.027	0.177	0.04	—
SAMPLING AREA 2—MOBILE BAY, ALA.							
Blue crabs	15	0.157	0.040	0.037	0.234	0.12	—
Shrimp	1.3 kg	0.006	0.002	0.003	0.011	0.01	—
Oysters	20+	0.042	0.004	0.003	0.049	0.03	—
Squid	10	—	—	—	—	0.04	—
Flounder	3	0.085	0.017	0.036	0.138	0.11	—
Speckled sea trout	1	0.710	0.170	0.280	1.160	0.40	—
Spanish mackerel	2	0.020	0.008	0.014	0.042	0.18	—

TABLE 2.—*Mirex, DDT and metabolites, and PCB residues in seafood*[1]—Continued

Species	Sample quantity	Residues in ppm					
		DDE	TDE	DDT	Total DDT & Metabolites	Aroclor 1260	Mirex
Weak fish	5	0.297	0.078	0.127	0.502	0.37	—
Atlantic whiting	5	0.052	0.010	0.008	0.070	0.11	—
Croaker	3	0.164	0.038	0.034	0.236	0.33	—
Red snapper	2	0.023	—	0.063	0.086	0.14	—
Mullet	5	0.260	0.150	0.111	0.521	0.11	—
Anchovy	>20	0.044	0.050	0.033	0.127	0.08	—
Shad	>10	0.669	0.030	0.045	0.744	0.09	—
SAMPLING AREA 3—TAMPA BAY, FLA.							
Crabs	10	0.027	0.004	0.014	0.045	0.03	—
Weak fish	5	0.075	0.033	0.082	0.190	0.83	—
Mullet	5	0.071	0.051	0.045	0.167	0.31	—
SAMPLING AREA 4—JACKSONVILLE, FLA.							
Blue crabs	15	0.011	0.011	0.035	0.057	0.08	—
Shrimp	1 kg	0.006	0.014	0.029	0.049	0.60	—
Flounder	3	0.162	0.128	0.524	0.814	0.65	—
Weak fish	5	0.067	0.019	0.127	0.213	0.44	—
Gray snapper	2	0.007	—	—	0.007	—	—
Grouper	3	0.041	—	—	0.041	—	—
Drum	5	0.013	0.011	0.041	0.065	0.17	—
Croaker	5	0.015	—	—	0.015	—	—
SAMPLING AREA 5—SAVANNAH, GA.							
Blue crabs	16	0.023	—	—	0.023	—	0.014
Shrimp	0.5 kg	0.005	—	—	0.005	—	0.007
Pilot shrimp	0.5 kg	0.016	—	0.011	0.027	—	0.007
Oysters	15	0.009	—	—	0.009	—	—
Razorback clams	28	0.020	0.016	0.020	0.056	—	—
Squid	5	—	—	—	—	—	0.007
Flounder	4	0.014	—	0.004	0.018	—	0.005
Weak fish	1	0.020	0.006	0.014	0.040	—	0.024
Mullet	1	0.004	—	0.003	0.007	—	0.006
Shad	13	0.027	0.023	0.028	0.078	—	0.009
Other fish	5	0.041	0.032	0.034	0.107	—	0.014
SAMPLING AREA 6— CHARLESTON, S. C.							
Blue crabs	10	0.057	—	—	0.057	—	—
Shrimp	1 kg	0.015	—	—	0.015	0.02	—
Oysters	>15	0.017	—	—	0.017	—	—
Squid	>15	—	—	—	—	—	—
Croaker	1	0.042	0.008	0.004	0.054	—	—
Mullet	5	0.027	0.017	0.004	0.048	—	—
SAMPLING AREA 7—MOREHEAD CITY, N. C.							
Blue crabs	15	0.012	—	0.001	0.013	—	—
Shrimp	1 kg	0.001	—	0.001	0.002	—	—
Oysters	24	0.039	0.017	0.006	0.052	0.02	—
Clams	20	0.003	0.002	0.003	0.008	—	—
Scallops	12	0.002	—	0.006	0.010	—	—
Flounder	3	0.030	—	0.010	0.040	—	—
Spanish mackerel	2	0.050	—	0.060	0.110	—	—
Weak fish	2	0.080	—	0.120	0.200	—	—
Blue fish	2	0.132	—	0.101	0.233	—	—
Mullet	5	0.115	0.082	0.189	0.386	—	—
Other	10	0.010	0.004	0.008	0.022	—	—
Fish meal	0.5 kg	0.095	0.050	0.060	0.205	0.11	—
SAMPLING AREA 8—CHESAPEAKE BAY							
Blue crabs	25	0.019	0.011	0.012	0.042	0.02	—
Weak fish	3	0.459	0.177	0.172	0.798	0.49	—
Striped sea bass	3	0.027	0.005	0.011	0.043	0.02	—
Spot	5	0.017	0.018	0.028	0.053	0.10	—
Herring	10	0.006	0.006	0.006	0.018	—	—
SAMPLING AREA 9—DELAWARE BAY							
Blue crabs	15	0.128	0.056	0.046	0.230	0.13	—
Flounder	2	0.023	—	0.021	0.044	0.07	—
Weak fish	5	0.479	0.059	0.044	0.582	0.23	—
Striped bass	2	0.046	0.007	0.033	0.086	0.07	—
Mullet	5	0.800	0.180	0.120	1.100	0.21	—
Other	2	1.295	0.550	0.630	2.475	1.17	—
Croaker	1	0.060	0.030	0.060	0.150	0.50	—

[1] Minus sign (—) denotes no residues found at lowest level of detection: 0.001 ppm for DDT, 0.005 ppm for Mirex, 0.01 for Aroclor 1260.

RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Mirex Residues in Selected Estuaries of South Carolina—June 1972 [1]

P. W. Borthwick,[2] G. H. Cook,[2] and J. M. Patrick, Jr.[2]

ABSTRACT

Estuarine sediments, crabs, shrimps, and fishes were collected in June 1972 at eleven stations two years after aerial applications of mirex bait for control of fire ants in coastal areas near Charleston, S.C. These stations had previously been monitored (October 1969 to June 1971) when levels of mirex in animal samples were: crabs, 0-0.60 ppm; shrimps, 0-1.3 ppm; and fishes, 0-0.82 ppm.

The recent study showed that mirex was present in three species of fishes (white catfish, 0.021 ppm; bluegill, 0.047 ppm; carp, 0.12 ppm) and blue crabs (0.026 ppm) at two freshwater stations. However, mirex was not detected in 36 animal samples, most of which were taken from nine saline stations in the estuaries after a period of restricted use of the pesticide. Analysis of bottom sediment samples at all stations detected no mirex. The lower limit of detection for mirex was 0.01 ppm.

Introduction

In June 1972 samples of estuarine sediments, crabs, shrimps, and fishes were collected at 11 stations near Charleston, S.C., where mirex fire ant bait had been applied aerially to coastal areas from October 1969 to December 1970. The United States Department of Agriculture supervised two applications of mirex, by fixed-wing aircraft, to several hundred thousand acres in the Charleston area. Treatments were terminated approximately 24 months before the June 1972 collections. However, 18 months lapsed since special applications were made by helicopter to 1200 acres at Toogoodoo Creek: Stations A, B, C, and D; and by hand seeder around a one-acre pond at Riverland Terrace: Station 1 (Fig. 1).

Since 1970 less extensive applications have been made for control of nuisance populations of fire ants. During the 1971-72 cooperative Federal State Control Program, mirex bait was applied aerially in South Carolina and seven other Southeastern states at property owners' requests.

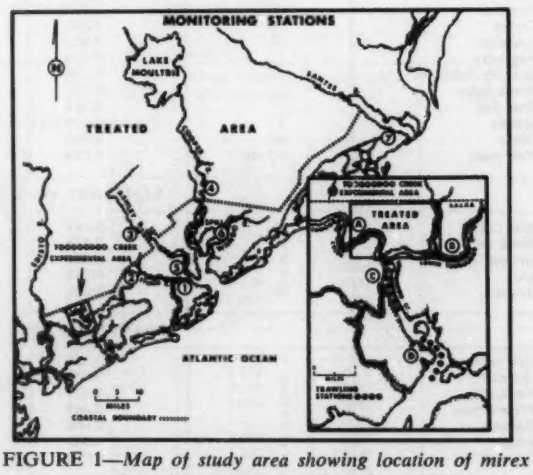

FIGURE 1—*Map of study area showing location of mirex sampling sites, South Carolina—June 1972*

[1] Contribution No. 168 from the Gulf Breeze Environmental Research Laboratory, United States Environmental Protection Agency, Gulf Breeze, Florida 32561; Associate Laboratory of the National Environmental Research Center, Corvallis, Oregon.

[2] Gulf Breeze Environmental Research Laboratory, Gulf Breeze, Florida 32561.

The use of mirex decreased when the U.S. Environmental Protection Agency (U.S. EPA) issued orders (*1, 2*) to cancel the registration of products containing mirex, pending relabeling. The orders required that no mirex be applied aerially near estuaries and other aquatic areas, wildlife refuges, or heavily forested areas. The present study was implemented to determine how much mirex remained in the estuarine fishes and crustaceans following a period of restricted use of the pesticide.

The stations (Fig. 1) and analytical techniques were identical to those used in a more comprehensive study of the area (*3*). Samples were collected and analyzed by the United States Environmental Protection Agency, Gulf Breeze Environmental Research Laboratory, Gulf Breeze, Florida.

Results and Discussion

In June 1972, 24 months after large-scale aerial treatment of inland areas, mirex residues greater than 0.01 ppm were found in only 4 of 40 animal samples (Table 1). All four samples were collected at the two freshwater stations located on the Ashley and Cooper Rivers (Stations 3 and 4, Fig. 1) which drain watersheds within the treated area. Three species of freshwater fishes and blue crabs contained the following amounts of mirex (ppm):

white catfish	0.021
bluegill	0.047
carp	0.12
blue crabs	0.026

Except for the bluegill, these animals are omnivorous bottom-dwellers. Blue crabs are euryhaline; they occasionally enter brackish and fresh waters of estuaries.

Mirex was not detected (Table 1) in the remaining 36 animal samples, most of which were taken at 9 stations located on tidal creeks in salt marsh areas that support populations of finfish and crustaceans. Many of these animals are transient and spend only a portion of their lives in the estuary. No mirex was detected in bottom sediments sampled at each location.

The lower limit of detection for mirex with the method employed (*3*) was 0.01 ppm.

Between October 1969 and June 1971 mirex residues in economically important members of the estuarine food chain varied as follows: crabs, 0-0.60 ppm; shrimps, 0-1.3 ppm; and fishes, 0-0.82 ppm. Levels of mirex in these species diminished to less than 0.01 ppm over a period of 18 to 24 months after the last aerial broadcast treatments to coastal South Carolina.

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TABLE 1.—*Whole body mirex residues, ppm, in estuarine animals, and sediments of South Carolina—June 1972*

Station Location:	Toogoodoo Creek				River-land Terrace Pond	Stono River	Upper [2] Ashley River	Cooper [2] River	Lower Ashley River	Wando River	South Santee River
Species / Station Identification:	A	B	C	D	1	2	3	4	5	6	7
CRABS											
Callinectes sapidus (blue crab)	—[1]	—	—	—	—	—	—	0.026	—	—	—
Uca pugilator (sand fiddler)			—								
SHRIMPS											
Penaeus aztecus (brown shrimp)	—	—	—	—	—	—		—	—	—	—
Palaemonetes pugio (grass shrimp)					—						
FISHES											
Leiostomus xanthurus (spot)	—		—	—	—	—	—	—	—	—	
Bairdiella chrysura (silver perch)		—						—			—
Ictalurus catus (white catfish)							0.021				
Cyprinus carpio (carp)								0.12			
Lepomis macrochirus (bluegill)							0.047				
MOLLUSKS											
Crassostrea virginica (oyster)			—								
Mercenaria mercenaria (hard clam)								—			
SEDIMENT	—	—	—	—	—	—	—	—	—	—	—

[1] — indicates <0.01 ppm mirex.
[2] Freshwater stations.

Monitoring 2,4-D Residues at Loxahatchee National Wildlife Refuge

Donald P. Schultz[1] and Eugene W. Whitney[2]

ABSTRACT

Over 7,000 acres along the Hillsboro perimeter canal in Loxahatchee National Wildlife Refuge (NWR), Florida, were sprayed in 1971 with the dodecyl-tetradecyl amine salts of 2,4-D (DTA-2,4-D) at a rate of 4.48 kg acid equivalent (a.e.) per hectare to control waterhyacinth (Eichornia crassipes). *Three stations were established along the canal to collect samples of fish, water, and mud for residue analysis and to monitor water quality.*

The initial application of 2,4-D, followed by spot treatments of DTA-2,4-D and/or the dimethylamine salt of 2,4-D (DMA-2,4-D) over a 4-month period, achieved excellent control of waterhyacinth. The highest 2,4-D residue level measured in water (0.037 mg/l) was found on the day following the initial treatment. The highest levels in hydrosol (0.005 mg/kg) occurred 3 to 15 days after treatment. Among 60 samples of fish, 3 had herbicide residue levels greater than 0.010 mg/kg, 16 had less than 0.010 mg/kg, and the remainder had no detectable residue levels. Breast muscle and liver of common Florida gallinules (Gallinula chloropus) *had residue levels of 0.30 mg/kg and 0.675 mg/kg, respectively, 1 day after spraying, and no detectable residues 4 days after spraying. The herbicide apparently caused no ill effects on hatching of boat-tailed grackle* (Cassidix mexicanus) *eggs or development of fledglings.*

Introduction

The Loxahatchee National Wildlife Refuge, located in southern Florida, consists of 143,000 acres of wetlands in the Florida Everglades. It is encircled by a 56-mile dike, and serves as a freshwater storage impoundment in the intricate water control system operated by the U.S. Army Corps of Engineers and South Florida Flood Control District. Hillsboro Canal, a perimeter canal which was created by excavation for dike fill, parallels the inner side of the dike. It contains open water all year, and is used extensively for sport fishing. The refuge supports over 180 species of birds and is important in the preservation of such endangered species as the Florida Everglade kite (*Rostrhamus sociabilis*), great white heron (*Ardea occidentalis*), and American alligator (*Alligator mississipiensis*).

Over the past several years, waterhyacinth (*Eichornia crassipes*) has become entrenched to varying degrees in the canal. There have been numerous occasions when the canal was completely blocked by the plant, thus curtailing public use of the Refuge for fishing, waterfowl hunting, and bird watching. In addition, a small amount of feeding habitat for the Florida Everglade kite was lost since the kite requires open water to see and capture the snail which is the mainstay of its diet.

In order to maintain the desirable features of the Refuge, the Division of Refuges, Bureau of Sport Fisheries and Wildlife, U.S. Department of the Interior, decided in 1971 to control the waterhyacinth in the perimeter canal and its proximity by spraying the hyacinth with the dodecyl-tetradecyl amine salts of 2,4-D (Emulsamine-3, Amchem Products, Inc., Ambler, Pa.) at the recommended rate of 4.48 kg acid equivalent (a.e.) per hectare (4 lb/acre) (John Gallagher, Amchem Products, Inc., Ambler, Pa. 1971. *Personal communication*).

Mullison (*1*) has reviewed many articles dealing with the toxicity of 2,4-D to aquatic organisms and levels of 2,4-D residues in aquatic environments. However, no published reports are available pertaining to the DTA-2,4-D formulation. Therefore, a monitoring program was designed to obtain data that would support registration of DTA-2,4-D for use on waterhyacinths at Loxahatch-

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ee NWR. This program was designed to obtain residue data from fish, water, and hydrosol, and to visually assess possible effects of the herbicidal applications on certain birds found in the Refuge.

Methods and Materials

Most of the herbicide was applied June 16-17 by a helicopter equipped with a microfoil boom. Spot treatments by airboat or helicopter were completed by October 15 to eliminate hyacinths that had not been killed in June. When the airboat was used, the 2,4-D formulation was the dimethylamine salt as opposed to the dodecyl-tetradecyl amine salts used in helicopter applications.

Three stations approximately 3 miles apart were established along the Hillsboro Canal (Fig. 1). Pretreatment samples of water, mud, and fish were taken in May 1971. Samples of fish, water, and mud for residue analysis were taken from each station at regular intervals after spraying.

Fish were obtained by gill netting. Fish samples were wrapped in aluminum foil, placed in plastic bags, frozen on dry ice, and kept frozen until residue analyses could be performed.

Water samples were a composite of shallow, medium, and deep water from each station. The samples were put in quart jars and acidified to about pH 1.5 with concentrated sulfuric acid; jars were capped with aluminum foil and screw caps. Hydrosol samples were a composite of three samples from each station, and were obtained with an Ekman dredge. These samples were placed in plastic bags, frozen on dry ice, and kept frozen until analyzed.

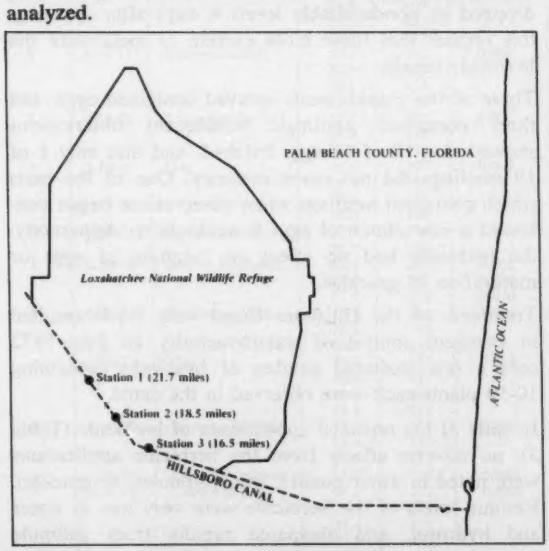

FIGURE 1.—*Location of sampling stations at Loxahatchee National Wildlife Refuge.*

Florida gallinules were killed by shotgun on six different occasions: once before initial treatment and five times afterward. All but one of the six samples consisted of three birds. The birds were wrapped in aluminum foil, bagged, and frozen until analyses were performed.

Six grackle nests containing eggs or young were located and permanently marked before spraying began. All the nests were in one colony in reeds immediately adjacent to a large clump of hyacinths, and were directly sprayed during treatment. Observations were made on hatching success and fledgling mortality for 6 weeks after spraying.

Dissolved oxygen content, pH, temperature, and water-hardness were determined by standard chemical or physical techniques (*2*).

Residue determination procedures for water, hydrosol, fish, and gallinules are given in Supplements A, B, C, and D. All solvents used were glass-distilled. Results were not corrected for percent recovery.

Results and Discussion

Physical and chemical parameters of the water and the quantities of 2,4-D residues found in the water and hydrosol are listed in Table 1. Fluctuations in dissolved oxygen content and pH could not be correlated with herbicidal application, and may have resulted from diurnal variations and the bloom and decay of algae.

The highest 2,4-D residue level in water was 0.037 mg/liter found 1 day after the initial treatment at Station 2. Water from Station 1 contained 0.016 mg/liter 1 day after treatment, but all other samples contained less than 0.010 mg/liter. There have been no published reports of DTA-2,4-D residues in water or hydrosol. Smith and Isom (*3*) found residues of 0.068 mg/liter of the butoxyethanol ester of 2,4-D (BEE-2,4-D) 8 hours after treatment at 40 to 100 lb of 2,4-D a.e. per acre in a Tennessee Valley Authority reservoir. Wojtalik et al. (*4*) found residues of 1.8 mg/liter 24 hours after application of 40 lb a.e. per acre of DMA-2,4-D. Both reports dealt with treatment of a submersed aquatic plant (*Myriophyllum spicatum*).

In our study, the target was thick mats of floating water-hyacinths. These plants intercepted much of the herbicide that otherwise would have entered the water. This interception partly explains the low residue levels found in water.

Only three hydrosol samples from Loxahatchee NWR contained detectable levels of 2,4-D (Table 1). None of these residues exceeded 0.005 mg/kg. In contrast, Smith and Isom (*3*) reported residues of 56 mg/kg BEE-2,4-D 96 hours after treatment at one sampling station. As with residue levels in water, absorption of the herbicide by the waterhyacinth mat was probably one reason we found such low residues in hydrosol.

TABLE 1.—*Analyses of water and hydrosol samples from Loxahatchee National Wildlife Refuge*

Station	Date	Water [1]						Hydrosol [2]
		Days after treatment	Temp, °C	Dissolved oxygen, mg/L	pH	Total hardness, mg/L	2,4-D, mg/L	2,4-D, mg/kg
1	4-27-71	0	26	5.6	7.3	200	0.000	0.000
1	6-17-71	1	30	8.0	7.4	250	0.016	0.000
1	6-19-71	3	27	7.9	7.6	250	<0.001	<0.005
1	6-20-71	4	— [3]	—	—	—	<0.001	<0.005
1	6-24-71	8	27	9.0	7.6	240	0.008	—
1	7-1-71	15	30	11.0	7.4	250	0.002	0.000
1	7-15-71	29	30	6.0	8.2	250	0.002	0.000
1	8-12-71	57	27	6.0	7.8	270	0.004	0.000
1	10-7-71	113	28	8.0	7.5	360	—	0.000
2	6-18-71	1	—	—	—	—	0.003	0.000
2	6-20-71	3	28	7.2	7.8	230	—	0.000
2	6-24-71	7	—	—	—	—	<0.001	0.000
2	7-2-71	15	29	11.0	7.4	240	<0.001	<0.005
2	7-15-71	28	31	6.0	8.2	240	<0.001	0.000
2	8-12-71	56	28	6.0	7.8	270	0.001	0.000
2	10-7-71	112	28	5.0	7.3	300	—	0.000
3	4-28-71	0	30	7.5	7.0	230	—	0.000
3	6-18-71	1	31	9.5	7.6	280	0.000	0.000
3	6-20-71	3	29	8.7	7.9	240	0.001	—
3	6-24-71	7	28	7.4	7.8	280	0.007	0.000
3	7-2-71	15	29	9.0	7.4	260	0.002	0.000
3	7-15-71	28	32	8.0	8.2	260	0.002	0.000
3	8-12-71	56	29	12.0	8.0	270	<0.001	0.000
3	10-7-71	112	30	8.0	7.6	300	—	0.000

[1] 250 ml water used for analysis through 8 days; 500 ml thereafter. [2] 70 g hydrosol used for all analyses. [3] Dashed line denotes no sample.

Other factors which may affect residue levels are photodecomposition and metabolism of the herbicide. For example, Aly and Faust (*5*) reported a photodecomposition loss of 50% of a sodium salt of 2,4-D in 50 minutes at pH 7.0. Also, Loos (*6*) and Menzie (*7*) reported in their reviews of 2,4-D metabolism that many microorganisms are capable of degrading 2,4-D. Hence, the disappearance of 2,4-D residues from water and hydrosol at Loxahatchee NWR probably was due to absorption, photolysis, and metabolism of the herbicide.

Data regarding 2,4-D residues in various sizes and species of fish and the station where fish were collected are given in Table 2. Usually, fish of the same species from the same collecting date and station were composited for residue analysis. In two instances each fish was analyzed individually. Muscle tissue, which included small quantities of bones, skin, or scales, was analyzed for 2,4-D.

Sixty analyses were made using a total of 193 fish. Only 19 samples contained detectable 2,4-D residues. Of these 19 samples, 8 had residues less than 0.010 mg/kg; 7 had between 0.010 and 0.050 mg/kg; 1 had between 0.051 and 0.10 mg/kg; and 3 samples had residues greater than 0.10 mg/kg.

With one exception, all fish samples which contained residues of 2,4-D were collected from a station which had been sprayed within the preceding 3 days (Tables 2, 3).

Smith and Isom (*3*) reported that one sample of bluegills (*Lepomis macrochirus*) collected 50 days after treatment of a reservoir at 100 lb BEE-2,4-D a.e./acre contained a residue of 0.15 mg/kg. The remainder of their fish samples contained no residues or less than 0.14 mg/kg. Wojtalik et al. (*4*) reported residues in gizzard shad (*Dorosoma cepedianum*) of 0.34 mg/kg 4 weeks after treatment and 0.22 mg/kg 3 months after treatment at 40 lb DMA-2,4-D a.e./acre. All other posttreatment samples contained less than 0.010 mg/kg 2,4-D residue. Based on our results and other studies (*3,4*), fish do not accumulate high levels of 2,4-D residues regardless of the formulation and concentration applied.

Physical and residue data from Florida gallinules are shown in Table 4. Levels of 2,4-D in breast muscle and liver in birds harvested 1 day after the initial spraying were 0.30 mg/kg and 0.675 mg/kg, respectively, but dropped to nondetectable levels 4 days after spraying; this implies that these birds excrete or metabolize the herbicide rapidly.

Three of the grackle nests sprayed contained eggs, and three contained nestlings. Subsequent observations showed that 10 of 11 eggs hatched, and that only 1 of 19 nestlings did not reach maturity. One of the nests which contained nestlings when observations began contained a new clutch of eggs 6 weeks later. Apparently, the herbicide had no effect on hatching of eggs or maturation of grackles.

Treatment of the Hillsboro Canal with 2,4-D resulted in excellent control of waterhyacinths. In July 1972 only a few scattered patches of hyacinths containing 10-50 plants each were observed in the canal.

In spite of the repeated applications of herbicide (Table 3), no adverse effects from the herbicide applications were noted in water quality, fish, gallinules, or grackles. Residue levels of the herbicide were very low in water and hydrosol, and dissipated rapidly from gallinule breast muscle and liver, and appeared to have no effect on grackle nestlings or hatching of eggs.

TABLE 2.—*Residues of 2,4-D in fish from Loxahatchee National Wildlife Refuge*

Station	Date	Species	Length, cm	Weight, g	Residues of 2,4-D, mg/kg [1]
1	4-27-71	Redear sunfish (*Lepomis microlophus*)	17.8	91	0.000
			15.2	45	
1	4-28-71	Largemouth bass (*Micropterus salmoides*)	28.0	227	0.000
			28.0	228	
1	4-28-71	Brown bullhead (*Ictalurus nebulosus*)	30.5	454	0.000
			25.4	227	
1	4-28-71	Gar (*Lepisosteus spp.*)	35.6	182	0.000
			33.0	136	
			30.5	91	
			38.1	182	
			48.3	454	
3	4-28-71	Chubsuckers (*Erimyzon spp.*)	33.0	368	0.000
			27.9	272	
			27.9	272	
3	4-28-71	Largemouth bass	27.9	227	0.000
			25.4	182	
3	4-28-71	Redear sunfish	20.3	227	0.000
			20.3	227	
			17.8	136	
1	6-17-71	Redear sunfish	17.8	91	0.101
			17.8	91	
			17.8	91	
			17.8	91	
1	6-17-71	Brown bullhead	27.9	343	0.012
			25.4	227	
			30.5	454	
			22.9	182	
			22.9	182	
2	6-18-71	Chubsuckers	30.5	454	0.000
			25.4	227	
			25.4	227	
			27.9	272	
			22.9	91	
2	6-18-71	Gar	45.7	454	0.000
			38.1	136	
			45.7	368	
			33.0	91	
			35.6	182	
2	6-18-71	Redear sunfish	20.3	182	0.000
			17.8	136	
			17.8	91	
			22.9	272	
			17.8	91	
3	6-18-71	Chubsuckers	33.0	590	<0.010
			33.0	454	
			30.5	409	
			27.9	227	
			27.9	227	
3	6-18-71	Redear sunfish	22.9	182	0.000
			22.9	182	
			20.3	136	
			17.8	91	
3	6-18-71	Largemouth bass	35.6	454	0.000
			27.9	318	
			27.9	318	
1	6-19-71	Gar	40.6	227	0.000
			48.3	454	
			55.9	454	
			33.0	136	
1	6-19-71	Redear sunfish	22.9	227	<0.010
			20.3	136	
1	6-19-71	Brown bullhead	25.4	227	0.000
			25.4	227	0.000
			27.9	318	0.000
2	6-20-71	Redear sunfish	22.9	272	0.000
			15.2	46	
			20.3	136	
2	6-20-71	Gar	55.9	727	0.028
			40.6	227	
			48.3	368	
			38.1	227	
2	6-20-71	Brown bullhead	27.9	272	0.000
			25.4	227	
			27.9	227	
3	6-20-71	Largemouth bass	27.9	227	0.000
3	6-20-71	Chubsuckers	25.4	272	0.000
			27.9	272	
			25.4	272	
			22.9	182	
			25.4	227	
			25.4	227	
3	6-20-71	Gar	38.1	227	0.022
			33.0	136	
			63.5	1090	
			45.7	368	
			43.2	368	
1	6-20-71	Redear sunfish	20.3	—	0.000
3	6-24-71	Gar	38.1	590	0.000
			35.6	545	
3	6-24-71	Chubsuckers	27.9	368	0.000
			30.5	409	0.000
			25.4	318	0.000
			25.4	318	0.000
			27.9	368	0.000
1	7-1-71	Redear sunfish	21.5	227	0.022
			17.8	113	
2	7-2-71	Chubsuckers	33.0	499	0.000
			30.5	454	
2	7-2-71	Redear sunfish	20.3	182	0.000
			25.4	272	
2	7-2-71	Bluegill (*Lepomis macrochirus*)	22.9	182	0.000
			20.3	182	
			22.9	227	
			20.3	182	
3	7-2-71	Redear sunfish	20.3	182	0.010
			20.3	182	
3	7-2-71	Chubsuckers	33.0	454	<0.010
1	7-15-71	Bluegill	20.3	136	0.000
			20.3	227	
			18.9	113	
1	7-15-71	Redear sunfish	18.9	113	0.000
			22.9	294	
2	7-15-71	Chubsuckers	30.5	454	0.000
			33.0	567	
2	7-15-71	Bluegill	17.8	227	<0.010
			17.8	204	
			20.3	227	
			20.3	227	
			20.3	227	
3	7-15-71	Bluegill	17.8	113	0.000
			20.3	227	
			22.9	340	
			17.8	182	
			22.9	227	
1	8-12-71	Gar	38.1	136	0.106
			48.3	454	
			43.2	272	
1	8-12-71	Brown bullhead	38.1	681	<0.010
			30.5	318	
			27.9	272	
1	8-12-71	Redear sunfish	17.8	91	<0.010
			17.8	91	
			17.8	91	
			17.8	91	
			17.8	91	
1	8-12-71	Chubsuckers	25.4	227	<0.010
			27.9	272	
			27.9	318	
			25.4	227	
			27.9	318	
2	8-12-71	Redear sunfish	22.9	227	0.162
			22.9	227	
			17.8	91	
			22.9	227	
			17.8	91	
3	8-12-71	Chubsuckers	30.5	454	0.000
			33.0	567	
			25.4	227	
			27.9	272	
			25.4	227	
3	8-12-71	Largemouth bass	27.9	227	0.012
			27.9	272	
			27.9	227	
			27.9	368	
			30.5	368	
3	8-12-71	Redear sunfish	20.3	227	0.024
			20.3	227	
			22.9	368	
			17.8	136	
			17.8	136	
1	10-7-71	Brown bullhead	30.5	368	0.000
			34.3	545	
			35.6	681	
			38.1	681	

TABLE 2.—*Residues of 2,4-D in fish from Loxahatchee National Wildlife Refuge*—Continued

Station	Date	Species	Length, cm	Weight, g	Residues of 2,4-D, mg/kg [1]
1	10-7-71	Gar	63.5	1362	0.000
			66.1	1544	
1	10-7-71	Redear sunfish	20.5	227	0.000
			20.3	182	
			20.3	227	
			19.1	182	
			24.2	368	
2	10-7-71	Redear sunfish	22.3	227	<0.010
			21.6	227	
			21.6	227	
			22.9	318	
			22.0	182	
2	10-7-71	Chubsuckers	36.9	726	0.000
			35.6	681	
			26.7	272	
			34.3	636	
			35.6	681	
3	10-7-71	Largemouth bass	35.6	636	0.000
			30.5	409	
			29.2	318	
			30.5	409	
			33.0	590	
3	10-7-71	Redear sunfish	22.9	227	0.070
			22.9	227	
			21.6	227	
			21.6	227	
3	10-7-71	Chubsuckers	33.0	545	0.000
			35.6	772	
			33.0	590	
			33.0	636	

[1] When only one set of data is given for a series of fish, the fish were composited for analysis.

TABLE 3.—*Spray schedule for Loxahatchee National Wildlife Refuge*[1]

Date	Area Sprayed	Method [2]	Acreage
6-1-71	Vicinity of Station 3	Boat	8
6-2-71	Stations 1, 2, 3	Boat	4
6-16-71	Station 1	Air	53.6
6-17-71	Stations 2, 3	Air	105.0
6-18-71	Between Stations 1 and 2	Air	105.0
6-21-71	Vicinity of Station 1	Boat	1.5
6-22-71	Vicinity of Station 1	Boat	4.5
6-22-71	Vicinity of Station 1	Air	84.2
6-23-71	Station 2	Air	105.0
7-1-71	Station 3	Boat	10
7-2-71	Vicinity of Station 3	Boat	6.0
7-9-71	Vicinity of Station 3	Boat	8.0
7-12-71	Stations 2 and 3	Boat	10.0
7-26-71	Stations 1 and 2	Air	95.0
7-27-71	Station 2	Air	105.0
7-28-71	Vicinity of Station 3	Boat	13.5
8-3-71	Vicinity of Station 1	Boat	12.0
8-3-71	Vicinity of Station 2	Air	23.3
8-4-71	Station 2	Air	105.0
8-4-71	Vicinity of Station 1	Boat	9.0
8-5-71	Between Stations 2 and 3	Boat	12.0
8-5-71	Vicinity of Stations 1-3 (flats)	Air	105.0
8-6-71	Station 1 (flats)	Air	105.0
8-6-71	Between Stations 2 and 3	Boat	8.0
8-9-71	Between Stations 2 and 3	Boat	8.5
8-9-71	Station 2	Air	105.0
8-10-71	Station 2	Air	17.5
8-11-71	Stations 1-3 (flats)	Air	77.5
8-11-71	Vicinity of Station 1	Boat	7.5
8-12-71	Vicinity of Stations 1-3	Boat	6.0
8-12-71	Station 3	Boat	5.0
8-16-71	Vicinity of Station 2	Boat	6.0
8-17-71	Vicinity of Stations 1 and 2	Boat	3.0
10-7-71	Stations 1-3	Boat	6.0

[1] All herbicide was sprayed at the rate of 4 lb acid equivalent per acre.
[2] Herbicide applied by boat was the dimethylamine salt of 2,4-D. Aerial applications were the dodecyl-tetradecylamine salts of 2,4-D.

TABLE 4.—*Residues of 2,4-D found in breast muscle and liver of common Florida gallinules* (Gallinula chloropus)

Harvest date [1]	Weight of birds, g	Combined weight of breast muscle, g	Residues of 2,4-D, mg/kg	Combined weight of liver, g	Residues of 2,4-D, mg/kg
6-18-71	363	98.8	0.000	19.4	0.000
	317				
	389				
6-18-71	390	105.1	0.300	22.9	0.675
	358				
	460				
6-21-71	357	66.0	0.000	11.2	0.000
	373				
	396				
6-23-71	320	75.4	0.000	15.5	0.000
	314				
	271				
6-25-71	261	53.7	0.000	9.5	0.000
	283				

[1] Control birds harvested 0.5 miles from site of spraying.

Supplement A

Method for analysis of water samples for determining concentrations of 2,4-D acid equivalent of Dodecyl-Tetradecyl amine salts or dimethylamine salt of 2,4-D.

1. Acidify water samples at time of collecting to a pH of less than 2 with concentrated sulfuric acid.
2. Extract representative sample of water (250-500 ml) three times with 100 ml chloroform.
3. Evaporate chloroform in a 500-ml round-bottom flask just to dryness with a rotary evaporator (do not allow water bath to exceed 45° C).
4. Add 5 ml diazomethane to the residue in flask. Allow to sit several minutes at room temperature. Add one-half ml benzene to flask and evaporate excess diazomethane in a hot water bath (60-70°C). Do not allow benzene to evaporate (*8*).
5. Add 5 ml benzene to flask. Transfer esterified 2,4-D to cleanup column.
6. Quantify on gas chromatography. Recovery from spiked samples was 97.5 ± 2.5%.

Supplement B

Methods for analysis of hydrosol samples for determining concentrations of 2,4-D acid equivalent of dodecyl-tetradecyl amine salts or dimethylamine salt of 2,4-D.

1. Thaw samples. Place 70-g portion in stainless steel grinding flask.
2. Add the following mixture to the flask: 1.0 ml 20% sulfuric acid, 15 ml acetone, 25 ml petroleum ether, 100 ml diethyl ether, 10 g Celite 545 (Fisher Scientific, Inc.).
3. Grind mixture for 2 minutes at medium speed. Suction-filter liquid through Whatman #1 filter paper (use teflon cloth if hydrosol has high clay content).
4. Repeat procedure 2 and 3. Rinse flask and hydrosol with two 25-ml aliquots of diethyl ether:petroleum ether (1:1).

5. Pour filter flask contents into 1-liter separatory funnel. Rinse flask with 10-15 ml of diethyl ether: petroleum ether mixture and add to separatory funnel.
6. Partition filtrate with 100 ml 0.05 N NaOH. Check pH; if less than 10, add enough 6 N NaOH to bring pH to 10 or higher (*9*). Partition filtrate a second time with NaOH.
7. Acidify aqueous phase to a pH of less than 2 by dropwise addition of 20% H_2SO_4 (about 3 ml total).
8. Quantitatively transfer acidified aqueous phase to 1-liter separatory funnel.
9. Follow procedure as outlined for water samples beginning with step 2. Recovery from spiked samples was 90 ± 2.5%.

Supplement C

Method for analysis of fish and gallinule samples for determining concentrations of 2,4-D acid equivalent of dodecyltetradecyl aminé salts or diethylamine salt of 2,4-D.

1. Thaw fish sufficiently to remove head and viscera; thaw gallinules sufficiently to remove breast muscle and liver. Chop tissue into small pieces (ca. one-half-inch cubes) and grind to a fine powder with twice their weight of dry ice in a Waring blender. Allow dry ice to sublime in a freezer (*10*).
2. Weight out portion of tissue powder (usually 25 g), mix with 100 g anhydrous Na_2SO_4, and allow to stand for 45-60 minutes with occasional stirring until powder is dry.
3. Pack powder lightly in a glass column (22-mm inside diameter by 30 cm) fitted with a fritted glass disk. Elute column with 200 ml methanol:phosphoric acid (99:1, v/v) (*11*).
4. Place eluate in a 1-liter separatory funnel containing 500 ml deionized water, and adjust pH to 4.5.
5. Add 100 ml petroleum ether to separatory funnel and shake vigorously for 2 minutes. Draw off petroleum ether, and repeat the ether extraction two more times.
6. Acidify water-methanol mixture to a pH of 1.5 with concentrated H_2SO_4. Extract mixture three times with 100-ml portions of diethyl ether.
7. Pass diethyl ether extract through glass column containing 12 cm anhydrous Na_2SO_4, and collect ether in a 500-ml round-bottom flask.
8. Evaporate ether just to dryness on a rotary evaporator.
9. Follow procedure as outlined for water samples beginning with step 4. Recovery from spiked samples was 90 ± 2.5%.

Note: if large quantities of fat or pigment are present in extracts, a preliminary extraction before step 4 may be done by putting the methanol-water extract into water adjusted to pH 8 with sodium bicarbonate and extracting with petroleum ether. The aqueous extract may then be adjusted to pH 4.5 and extracted with petroleum ether.

Caution! There will be violent gas evolution at this stage.

Supplement D

Procedure for cleaning up 2,4-D acid residues derivatized with diazomethane.

1. Place glass-wool plug in bottom of glass column (22-mm inside diameter by 30 cm). Add 8 cm silica gel (Brinkman #7754, Brinkman Instruments, Inc., Cantiague Road, Westbury, New York 11590) and 2 cm anhydrous Na_2SO_4.
2. Rinse column with 150 ml benzene. Discard eluate. Quantitatively transfer 2,4-D methyl ester from round-bottom flask to top of column.
3. Elute column with 180 ml of 2% diethyl ether in benzene. Collect eluate in porcelain casserole and evaporate to a small volume on a hot plate in a hood.
4. Transfer 2,4-D methyl ester to suitable container, and bring up to volume for analysis by gas chromatography.

The gas chromatograph used for the residue analyses was a Perkin-Elmer Model 800 equipped with a Tracor Electrolytic Conductivity Detector. The column was coiled glass, 6-ft-by-⅛-inch inside diameter, packed with 10% DC-200 on Gas-Chrom Q (80-100 mesh). Column temperature was 180° C, injector temperature 220° C, venting block 265° C, and pyrolysis furnace 840° C. Retention time for the methyl ester of 2,4-D under these conditions was about 2.2 minutes.

Detection limit of the 2,4-D methyl ester was 1.25 ng with 15 ng giving a 50% deflection on the recorder. Detection limit for fish samples: 0.01 mg/kg; for hydrosol: 0.005 mg/kg; and water: 0.001 mg/liter.

Confirmatory analyses of the 2,4-D methyl ester standard, spiked samples, and periodic samples were conducted by electron capture detection on a Beckman GC-4 gas chromatograph.

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Nationwide Organochlorine and Mercury Residues in Wings of Adult Mallards and Black Ducks during the 1969-70 Hunting Season

Robert G. Heath[1] and Sharon A. Hill[2]

ABSTRACT

Nationwide monitoring of organochlorine and mercury residues in wings of approximately 5,200 adult mallards and black ducks bagged during the 1969-70 hunting season showed DDE, as in 1965 and 1966, to be the predominant residue. PCB's were next in overall prevalence, followed by mercury, DDT, dieldrin, DDD, and heptachlor epoxide. There was no indication of a decrease in levels from 1966. Residues were generally highest in the Atlantic and Pacific Flyways and lowest in the Central Flyway; PCB's, however, were highest in the Atlantic Flyway and diminished westward across the Nation. Mercury residues were highest in Atlantic Flyway black ducks. Monitoring results were consistent: States with high residues in 1965 and 1966 were again high in 1969. Analyses of individual wings of mallards from California and black ducks from New Jersey and New York revealed DDE residues as high as 41 ppm and certain regional and seasonal differences in levels within States. They also revealed an apparent tendency for DDE residues to be more variable and to attain higher levels in male than in female wings.

Introduction

The first nationwide monitoring of pesticides in waterfowl occurred in early 1966 when the U.S. Department of the Interior Bureau of Sport Fisheries and Wildlife assessed organochlorine residues in wings of approximately 12,000 mallards (*Anas platyrhynchos*) and black ducks (*Anas rubripes*) bagged during the 1965-66 hunting season. Monitoring was repeated a year later with a similar number of wings from the 1966-67 hunting season, and the data from the two years were combined to provide base readings for measuring trends in future residue levels (*1*). Monitoring was thereafter scheduled at 3-year intervals to serve this purpose. The undertaking is a segment of the National Pesticide Monitoring Program; the Bureau's current commitment in that program is described by Dustman et al. (*2*).

Wings of approximately 5,200 adult mallards and black ducks bagged during the 1969-70 hunting season have been monitored. Findings of that survey are presented in the following report, which includes: (a) average wing levels of DDE, DDT, DDD, dieldrin, PCB's, and mercury among birds bagged in each State; (b) a comparison of 1969-70 levels of DDE and dieldrin with the earlier 2-year averages (DDT and DDD comparisons are biased by earlier PCB interference); and (c) a special study of individual wings from California, New Jersey, and New York to compare residues among birds bagged in different periods and regions within each State.

The wings used in monitoring are a by-product of an established nationwide survey in which, each fall, selected waterfowl hunters mail the Bureau tens of thousands of duck wings for biological examination. An appraisal of their suitability as a medium for monitoring was presented earlier (*1,3*).

Methods

NATIONWIDE MONITORING

Wings from the 1969-70 waterfowl season were mailed by hunters to one of four regional collection points and held in frozen storage for biological examination in early 1970. Hunters reported the date, State, and county of kill for each wing, and biologists determined the species, sex, and maturity of the bird. Wings of adult mallards from most States, and of adult black ducks from eastern States, were retained for monitoring following biological examination.

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For practicality, monitoring in 1970 was restricted to adult wings; of those chemicals consistently detected in the earlier monitoring (DDE, DDT, DDD, and dieldrin), only DDE proved to have higher residues in adult wings than in immature wings. DDE levels in adults are of particular concern because the chemical has been shown experimentally to cause eggshell thinning in both mallards (*4, 5*) and black ducks (*6*).

As in earlier monitoring, the wings from each State were sorted systematically into pools of 25 each, and a random sample of pools roughly proportional in number to the State's mallard or black duck harvest was then selected for chemical analysis. Pools not selected were discarded except for certain mallard wings from California and black duck wings from New York and New Jersey which were retained for individual analyses (see *Findings*, this paper). Each pool or individual wing was enclosed with an individually numbered tag in a plastic bag, packaged in dry ice, and shipped for chemical analysis to WARF Institute, Inc., Madison, Wisconsin. Wing material was identified only by a code number during chemical analysis.

INDIVIDUAL WINGS

In earlier monitoring, variation in pool levels of DDE within certain States with the highest averages was sufficient to indicate that some birds carried residues considerably higher than the respective average. To investigate this likelihood, selected mallard wings from California and black duck wings from New Jersey and New York were analyzed individually to compare residues among birds bagged in different regions of the State and/or during different periods of the hunting season. Regions and periods were chosen, hopefully, to maximize any contrasts in levels. It was hypothesized that residues for these States would tend to be higher in birds taken early in the season when, prior to full-scale migration, the population comprised a higher proportion of local birds.

In California, wings were collected from three regions: a northeast region comprising Lassen, Siskyou, and Modoc Counties, a second region comprising the counties of the Sacramento Valley, and a third region comprising counties of the San Joaquin Valley. These areas were sampled October 18–November 15, 1969, and January 1-10, 1970. The northeast region, devoted largely to ranching, was expected to yield birds with residues lower than those in birds from the two Valley regions of intensive agriculture to the south.

Residues in black ducks from New Jersey and New York were investigated conjunctively with samples of 28 and 34 wings. In New Jersey, which was not regionalized, wing residues in birds from coastal counties bagged October 13-26 were compared with those bagged December 13-27. New York was regionalized into Long Island and upstate New York. To investigate whether residues were higher in birds from coastal New Jersey and Long Island than in birds from upstate New York, the latter were sampled October 13-26 for simultaneous comparison with New Jersey, and November 17-30 for comparison with birds bagged concurrently on Long Island.

CHEMICAL METHODOLOGY

Preparatory to analysis, wings were trimmed by removing the distal joint and most of the feathers. The remaining portions were chopped and blended into 25-wing homogenates with a Hobart food chopper. A 40-g aliquot of homogenate was removed for pesticide and PCB analysis, and a separate 10-g aliquot was taken for mercury analysis. The 40-g aliquot was dried at 40°C to constant weight, ground with anhydrous sodium sulfate, and extracted in a Soxhlet for 8 hours with 300 ml of a mixture (70:170) of ethyl ether:petroleum ether. The extract was eluted through a standardized Florisil column with 250 ml of a mixture (3:1) of hexane: benzene, partitioned into acetonitrile, and passed a second time through a Florisil column. The eluate was concentrated and made to volume. Half the Florisil eluate was used to measure organochlorine pesticides, and the second half was reserved for PCB analysis. Lipids were measured by drying a 25-ml aliquot of the Soxhlet extract.

Organochlorine pesticides were quantified as follows: Using thin-layer chromatography (TLC), samples were plated on glass-backed Chrom AR 7GF 20 x 20 prepoured plates. The pesticides and PCB's were developed and separated into four zones on each plate as described by Mulhern (*7*), except that hexane was used as the developing solvent instead of hexane:ethyl ether. Each zone was analyzed on a 3% OV-17 column, with confirmation on 5% DC-200 and 3% XE-60. Operating specifications are shown in Table 1.

TABLE 1.—*Chromatographic operating specifications using electron capture detection*

	COLUMNS: GLASS, 4-FT-BY-4-MM INSIDE DIAMETER		
Liquid Phase	3% OV-17	5% DC-200	3% XE-60
Support	Gas Chrom Q	Gas Chrom Q	Gas Chrom Q
Mesh size	100/120	80/100	60/80
Temperature	190°C	190°C	170°C
Retention time, minutes	3.5(dieldrin)	6-8(*p,p'*-DDT)	10-12(*p,p'*-DDT)

PCB determinations were derived using semiquantitative thin-layer methods (*8*), with the modification that 0.1 g instead of 1.0 g $AgNO_3$ was used in making the plates. All PCB samples were read by comparison of total area with an Aroclor 1254 standard.

Total mercury was determined by cold vapor atomic absorption. The 10-g aliquot was digested by refluxing

with a mixture of sulfuric and nitric acids (9). A mixture of hydroxylamine, stannous chloride, and sulfuric acid was added to the digest to reduce the mercury (II) ions to mercury metal. Samples were aerated (3 liters/min) and passed through the absorption cell.

All residues have been expressed on a wet-weight basis. Limits of sensitivity were 0.02 ppm for organochlorine pesticides, 0.03 ppm for total PCB's, and 0.05 ppm for mercury. Conversion of residue levels to ppm dry weight or ppm lipid weight may be approximated by dividing a given wet-weight value by 0.57 or by 0.13, the respective mean proportions of dry or lipid material in each sample. Precise measurements of dry and lipid proportions for specific samples are available upon request.

The recovery efficiency of the analytical procedures was evaluated by analyzing nine 40-g aliquots of homogenized wing material known to contain only trace quantities of residues. Three of the aliquots remained untreated, three were identically spiked with low levels of five chemicals, and three were spiked with high levels. Spiking included 0.5 ppm or 1.0 ppm *p,p'*-DDT, 0.1 ppm or 0.2 ppm *p,p'*-DDD, 3.0 ppm or 5.0 ppm *p,p'*-DDE, 0.06 ppm or 0.2 ppm dieldrin, and 0.5 ppm or 5.0 ppm PCB as Aroclor 1254. DDT was recovered at an estimated rate of 86%, DDD at 81%, DDE at 96%, dieldrin at 88%, and PCB at 123%. Recovery efficiency for mercury was 97%; the median difference among duplicate analyses of 15 pools was 0.01 ppm mercury, and the coefficient of variation was 22.7%. None of the reported residue data have been adjusted for rates of recovery.

Findings

NATIONWIDE MONITORING

Average residue levels (ppm wet weight) of DDE, DDT, DDD, dieldrin, PCB, and mercury in wings of adult mallards or black ducks in late 1969–early 1970 are listed in Table 2 by State where collected. The table also lists the 2-year averages (1965-66) for DDE and dieldrin, as well as the sample size, range, and standard error associated with each average. States are listed in north to south order within each of the waterfowl flyways (Atlantic, Mississippi, Central, and Pacific) to facilitate geographic comparisons. Table 3 lists the flyway averages for the same chemicals and periods, the averages having been derived by weighting each of the State averages by the estimated State bag of the species.

DDE again proved to be the predominant organochlorine residue in mallard and black duck wings. It was present in measurable amounts in every pool, ranging in concentrations from a low of 0.06 ppm in a mallard pool from Nebraska to a high of 5.27 ppm in a black duck pool from New Jersey. State DDE averages ranged from 0.09 ppm in South Dakota mallards to 3.42 ppm in New Jersey black ducks.

There was no indication that DDE levels were diminishing during the 3-year period from 1966 to 1969. Residues tended to remain stable in the Pacific and Central Flyways; an apparent increase in the latter was due largely to an unusually high Texas reading. DDE levels tended to have increased in mallards from the Mississippi and Atlantic Flyways; averages were higher in 18 of 21 States. Changes in DDE levels in black ducks were mixed, although there was a tendency for levels to be higher in 1969.

Geographically, State and regional contrasts in DDE levels seen in earlier wing monitoring were again prevalent. Levels in black ducks from the contiguous Atlantic Flyway States extending from New Hampshire to Delaware were among the highest in the survey, although increases in birds from Virginia, North Carolina, and South Carolina resulted in levels nearly as high as those to the north. The highest average DDE residues in the nation occurred in birds from New Jersey, where wings of black ducks averaged 3.42 ppm and mallards 2.62 ppm. Residues were again high in mallards from Alabama (1.75 ppm), California (1.52 ppm), Utah (1.29 ppm), Pennsylvania (1.48 ppm), and New York (0.99 ppm). Mallard wings from certain of the Central Flyway States (Montana, Wyoming, South Dakota, Nebraska, Kansas, and Oklahoma) again carried the lowest DDE residues, averaging from 0.09 ppm in South Dakota to 0.15 ppm in Oklahoma.

DDT residues averaged from approximately one-fifth to one-tenth as high as those of DDE, the highest DDT averages occurring in Utah mallards (0.28 ppm) and New Jersey black ducks (0.27 ppm). Residues of DDD seldom exceeded trace levels. DDT and DDD residues should not be compared with those from earlier wing monitoring, because interference from certain PCB isomers undoubtedly inflated the earlier readings.

Dieldrin levels in mallard wings showed little change from 1965 and 1966 monitoring. The apparent increase in black duck residues in the Atlantic Flyway could not be substantiated statistically because of variability in the data. The highest dieldrin levels were again found in wings from the Atlantic Flyway; the highest averages were in black ducks from Maine (0.44 ppm), Massachusetts (0.18 ppm), Connecticut (0.16 ppm), Rhode Island (0.26 ppm), and Pennsylvania (0.16 ppm). Dieldrin averaged 0.14 ppm in mallards from Pennsylvania, the only State of the above five from which mallards were sampled. Dieldrin averaged approximately 0.18 ppm among black ducks for the three-State area of Virginia and the Carolinas, although residue levels among pools varied more than in the northern group of States. In the remaining flyways, State dieldrin averages exceeded 0.05 ppm only in Ohio, Alabama, Arkansas,

Texas, and Utah. All States except Ohio had been noted for prevalence of dieldrin in previous wing monitoring.

Dieldrin and DDT levels were comparable in black ducks; whereas in mallards, dieldrin residues were nationwide somewhat less than those of DDT. With few exceptions, dieldrin residues exceeded those of DDD.

Heptachlor epoxide was detected in most pools and in every State except Vermont. Few pools contained levels exceeding 0.02 ppm; therefore the chemical was excluded from the tables. No other organochlorine residues of pesticidal origin were reported.

PCB levels exhibited pronounced geographic differences, being highest in the Atlantic Flyway and generally diminishing westward. Residues were highest from New Hampshire southward through Delaware. The highest average PCB levels in the entire survey were found in black ducks from Connecticut (3.88 ppm) and Massachusetts (2.12 ppm). State averages exceeded 0.50 ppm throughout the Atlantic Flyway except in black ducks from Maryland (0.39 ppm). PCB levels in the Mississippi Flyway were highest in birds from States bordering the Great Lakes, diminishing southward in all States except Tennessee. Levels were comparably lower in the Central and Pacific Flyways, averaging overall about 0.15 ppm. The relatively high Nevada average (0.73 ppm) needs further investigation, and the low California average (0.04 ppm) may reflect the fact that there is little heavy industry in that part of the State most frequented by mallards.

Mercury residues of at least 0.05 ppm were detected in all pools of wings. However, levels exceeded 0.50 ppm in only three pools, one each from New York (black ducks, 0.80 ppm), Wisconsin (1.0 ppm), and Nevada (0.55 ppm). Mercury levels in mallards were comparable in all flyways, averaging about 0.10 ppm. Black ducks from the Atlantic Flyway averaged nearly double this level of mercury; averages were slightly higher from Delaware northward.

INDIVIDUAL WINGS, CALIFORNIA

In the following comparisons of residues in wings of individual mallards from California, sexes have been segregated (Table 4). Residues, especially DDE, in a given group of wings tended to be more variable and exhibit higher levels in male than in female wings, although females might have the higher median level. Because underlying statistical distributions were not well understood, all tests of significance have been based on nonparametric methods (*10, 11*).

In California, as hypothesized, DDE residues in certain mallard wings greatly exceeded the State mean of 1.52 ppm (Table 4). There were also demonstrable differences in average DDE levels between certain seasonal and regional groups of wings. Levels were highest in the sample of 11 Sacramento Valley males taken during the early period, when the highest proportion of local birds was expected to be in the population; levels ranged from 0.49 ppm to 41.72 ppm, exceeding 3.40 ppm in 7 of 11 wings. To the south, residues in all six early-period males from the San Joaquin Valley exceeded 0.30 ppm, and one wing contained 20.10 ppm DDE. However, in the five early-period males from the northeast counties where ranching predominates, DDE did not exceed 0.30 ppm except in one wing (6.60 ppm). The difference between the average level for Sacramento Valley males and that for males from the northeast counties was statistically significant ($P = 0.05$), and the difference between San Joaquin County males and those from the northeast approached significance ($P < 0.10$). A significant difference could not be shown between the two Valley regions.

In parallel early-period comparisons of DDE residues in female wings, the average level for the San Joaquin Valley was significantly higher ($P < 0.01$) than that for the northeast counties. Comparisons involving Sacramento Valley females were restricted by a shortage of wings.

Regional comparisons of late-period DDE levels necessarily excluded the northeast region where wings were unavailable. The tendency for levels in late-period males to be higher in the San Joaquin Valley (range 0.32-30.65 ppm) than in the Sacramento Valley (0.18-7.13 ppm) was not statistically significant; there were not enough female wings for meaningful comparison.

Seasonal comparisons could be made only within the two Valley regions since late-period wings from the northeast counties were unavailable. In males from the Sacramento Valley, average DDE levels during the early period were significantly higher ($P<0.01$) than during the late period; levels in 7 of 12 wings from the late period were below the lowest level encountered among the 11 early-period wings. No similar difference was demonstrable in male wings from the San Joaquin Valley, perhaps because relatively fewer migrants winter in the San Joaquin Valley than in the Sacramento Valley. Female wings were too few in number for meaningful comparisons of seasonal differences within either Valley region.

DDE residues in female wings did not exhibit the extreme levels detected in males; differences were apparently due to more than the fact that the sample comprised 39 males compared to 21 females. DDE exceeded 3.00 ppm in only 2 of 21 female wings (4.67 and 3.79 ppm); however, residues exceeded 3.00 ppm in 13 of 39 male wings, the 4 highest of which were 41.72, 30.65, 20.10, and 12.37 ppm. Despite such values, median DDE levels were higher for females in three of the five regional—period groups.

INDIVIDUAL WINGS, NEW JERSEY AND NEW YORK

As with California mallards, sexes were segregated so far as possible in comparing wing residues among individual black ducks from New Jersey and New York (Table 5). Within the set of wings from a given region and period, DDE levels appeared to be higher in male wings than in wings from females or birds of unidentified sex, although differences were not statistically significant, nor so pronounced as in California mallards.

As hypothesized, DDE residues tended to be higher in wings of birds taken in coastal counties than in those from inland counties. The average DDE level in males sampled from coastal New Jersey October 17-26 was significantly higher ($P<0.01$) than in males from upstate New York during the same period: levels in six of nine New Jersey wings ranged from 3.04 to 13.79 ppm, whereas the highest level in eight New York wings was 2.20 ppm DDE. Similarly, levels in four males from Long Island bagged November 17-30 exceeded those in four males from upstate New York taken during the same period ($P<0.02$). The same comparisons for female wings showed tendencies similar to those for males, but differences were less pronounced and merely approached statistical significance. Seasonal differences in DDE levels could not be demonstrated either in New Jersey or in upstate New York; Long Island was sampled during only one period. For New Jersey, the average DDE level for males taken December 13-27 was numerically lower than for those bagged October 17-26, but the difference was not statistically significant. Female wings were inadequately represented for comparison.

Discussion

From the data in Table 2, a multitude of statistical comparisons of residue levels is possible both between States and between years within States. In many instances differences clearly are either significant or not significant. Caution is suggested, however, when the distinction is not clear-cut: the individual pool values may facilitate a more rigorous test of significance than is possible using pool means and their standard errors. Caution is also suggested in combining data from adjacent States unless the data have been properly weighted. Individual pool values and weighting factors are available on request.

The precision with which these wing monitoring data can be interpreted has been questioned at times because of the mobility of mallards and black ducks during migration and the subsequent difficulty in associating wing residues with specific geographic locations. The subject has been discussed in previous papers (*1*, *3*), but further elaboration is perhaps warranted.

The foremost objective in monitoring wings of mallards and black ducks is to quantify not only levels, but also trends in levels of pesticides and pollutants in continental populations of these highly valued waterfowl. Trends may be either in time or space. As stated earlier (*1*), "Essentially, we are monitoring flyway as well as State populations, the wings from each State being a sample of that part of a flyway population frequenting the State during the hunting season." It was also stated (*3*), ". . . the mobility of the species might permit only a general location of the source of contamination, [but] monitoring of localized material (soil, crops, etc.) by other agencies should help identify such concentrations." The same general problem exists in monitoring other motile media, whether air, flowing water, or a migratory species; however, a medium need hardly be fixed in space to warrant monitoring.

Several factors support the hypothesis of positive association between average residue levels in wings from a State and average levels in at least that portion of the State's aquatic environment frequented by waterfowl. These factors include consistency of wing monitoring data, consistency of migration patterns of adult ducks (*12*), and, in general, rapid dietary assimilation of organochlorine residues (*13*, *14*).

Summary

Nationwide monitoring of organochlorine compounds and mercury in wings of adult mallards and black ducks from the 1969-70 hunting season showed that all residues, except those of PCB's, were highest in the two coastal flyways, intermediate in the Mississippi Flyway, and lowest in the Central Flyway. PCB residues followed a similar pattern except in the Pacific Flyway, where residues were generally the lowest in the nation.

DDE was again the predominant residue. Average levels failed to suggest a decrease from 1966 and, in fact, increased in mallards in 18 of 21 States sampled in the Atlantic and Mississippi Flyways. No changes in dieldrin levels could be substantiated statistically, although the average level appeared to increase in the Atlantic Flyway. PCB and mercury were not previously quantified, and DDT and DDD should not be compared with earlier measurements because they undoubtedly include some PCB contamination.

Analyses of individual mallard wings from California and black duck wings from New Jersey and New York for residues of organochlorine pesticides revealed DDE residues as high as 41 ppm in the mallards and 13.8 ppm in black ducks, whereas the highest respective DDE levels among 25-wing pools were 2.70 ppm and 5.27 ppm. Analyses of individual wings from California showed that residues were higher in birds from the intensively cultivated Sacramento and San Joaquin Valleys than from the northeastern ranching counties. In New Jersey and New York, birds from the coastal counties contained significantly higher residues than did those

from upstate New York. In both instances the data suggest a tendency for residues to be more variable and attain higher levels in male than in female wings, although the median level might be higher in the female wings of a given set.

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(*13*) *Dindal, D. L. 1970.* Accumulation and excretion of Cl^{36} DDT in mallard and lesser scaup ducks. J. Wildl. Manage. 34(1): 74-92.

(*14*) *Stickel, W. H., L. F. Stickel, and F. B. Coon. 1970.* DDE and DDD residues correlated with mortality of experimental birds. Pp. 287-294 *In* Pesticides symposia, W. B. Deichmann, Ed. Helios and Assoc., Miami. xxxviii + 314 pp.

TABLE 2.—*Fall residue[1] levels of DDE, DDT, DDD, dieldrin, PCBs, and mercury in pools of 25 wings of adult mallards or black ducks: 1969 compared with 1965-66*

State; year	No. of pools	Residues, ppm (wet weight)															
		DDE			DDT			DDD			Dieldrin			PCB's			Mercury		
		Mean	Extreme values	Std. error	Mean	Extreme values	Std. error	Mean	Extreme values	Std. error	Mean	Extreme values	Std. error	Mean	Extreme values	Std. error	Mean	Extreme values	Std. error
BLACK DUCKS, ATLANTIC FLYWAY																			
Maine																			
1969	3	0.60	0.33-0.85	0.122	0.05	0.03-0.07	0.009	(0.01) [2]	all t [2]	(0.007)	0.44	t-1.72	0.426	0.79	0.20-1.64	0.332	0.19	0.16-0.24	0.017
1965-66	4 + 4	0.48	0.32-0.82	0.064							(0.02)	—	(0.006)						
Vt.																			
1969	2	0.66	0.60-0.71	0.055	0.03	0.03-0.03	0	(0.01)	all t	(0.010)	(0.01)	all t	(0.010)	0.83	0.33-1.33	0.500	0.26	0.14-0.39	0.125
1965-66	3 + 3	0.75	0.18-2.10	0.279							(0.02)	—	(0.008)						
N.H.																			
1969	2	0.87	0.80-0.93	0.065	0.04	t-0.06	0.025	(0.01)	all t	(0.010)	0.02	0.02-0.02	0	1.50	1.33-1.67	0.170	0.20	0.20-0.20	0
1965-66	3 + 3	0.88	0.48-2.17	0.262							0.10	n [4]-0.55	0.092						
Mass.																			
1969	4	1.90	1.11-2.34	0.286	0.09	t-0.19	0.038	0.04	0.02-0.05	0.007	0.18	0.05-0.49	0.105	2.12	1.64-3.00	0.303	0.22	0.21-0.22	0.003
1965-66	4 + 4	1.69	1.28-2.67	0.166							0.10	n-0.38	0.045						
Conn.																			
1969	3	1.06	0.98-1.22	0.078	0.13	0.09-0.16	0.022	0.02	0.02-0.03	0.003	0.16	0.08-0.22	0.042	3.88	2.67-5.00	0.674	0.21	0.19-0.24	0.017
1965-66	3 + 3	1.51	0.77-2.62	0.311							0.06	n-0.18	0.029						
R.I.																			
1969	3	1.36	1.27-1.45	0.052	0.18	0.15-0.24	0.029	0.03	0.02-0.03	0.003	0.26	0.23-0.29	0.018	1.58	1.00-1.96	0.295	0.19	0.14-0.22	0.024
1965-66	3 + 3	0.94	0.56-1.50	0.156							0.21	n [4]-0.43	0.061						
N.Y.																			
1969	4	1.19	0.90-1.69	0.174	0.13	0.02-0.23	0.043	0.02	0.02-0.03	0.003	0.03	0.02-0.04	0.004	1.64	0.25-3.00	0.578	0.33	0.18-0.80	0.157
1965-66	4 + 4	1.24	0.78-1.58	0.092							0.05	n-0.15	0.021						
Pa.																			
1969	3	0.78	0.70-0.91	0.067	0.06	0.04-0.07	0.009	(0.01) [2]	all t [2]	(0.007)	0.16	0.03-0.30	0.078	1.00	0.50-1.67	0.348	0.16	0.12-0.19	0.020
1965-66	3 + 3	1.14	0.33-3.60	0.511							(0.03)	n-0.10	(0.016)						
N.J.																			
1969	5	3.42	2.31-5.27	0.520	0.27	0.18-0.35	0.036	0.09	0.06-0.12	0.010	0.06	0.02-0.12	0.018	0.92	0.13-1.66	0.295	0.18	0.15-0.23	0.014
1965-66	5 + 5	2.10	1.32-3.45	0.228							(0.03)	n-0.08	(0.010)						
Del.																			
1969	2	1.54	1.52-1.55	0.015	0.12	0.11-0.12	0.005	0.04	0.03-0.04	0.005	0.03	0.03-0.03	0	1.06	0.62-1.50	0.440	0.20	0.15-0.25	0.050
1965-66	3 + 3	0.88	0.50-1.50	0.171							0.05	n-0.19	0.032						
Md.																			
1969	3	0.55	0.47-0.63	0.046	0.06	0.05-0.08	0.009	(0.01) [2]	all t [2]	(0.007)	0.03	0.02-0.03	0.003	0.39	0.10-0.83	0.223	0.11	0.10-0.13	0.009
1965-66	3 + 3	0.33	0.13-0.51	0.056							(0.03)	n [4]-0.06	(0.010)						
Va.																			
1969	3	0.89	0.64-1.18	0.157	0.14	0.04-0.30	0.081	0.02	t-0.03	0.006	0.13	t-0.32	0.096	1.17	0.50-2.00	0.441	0.15	0.13-0.17	0.012
1965-66	3 + 3	0.40	0.20-0.72	0.077							0.11	n-0.43	0.071						
N.C.																			
1969	2	0.80	0.74-0.86	0.060	0.08	0.06-0.09	0.015	0.02	0.02-0.03	0.005	0.30	0.03-0.57	0.270	0.66	0.49-0.83	0.170	0.15	0.14-0.16	0.010
1965-66	1 + 2	0.48	0.31-0.66	0.101							(0.02)	—	(0.017)						
S.C.																			
1969	2	1.03	0.76-1.30	0.270	0.06	0.05-0.07	0.010	0.03	0.02-0.04	0.010	0.10	0.06-0.15	0.045	1.25	0.50-2.00	0.750	0.18	0.18-0.19	0.005
1965-66	2 + 2	0.30	0.18-0.53	0.081							(0.03)	n-0.07	(0.017)						
MALLARDS, ATLANTIC FLYWAY																			
N.Y.																			
1969	3	0.99	0.86-1.11	0.072	0.10	0.07-0.14	0.020	0.02	0.02-0.03	0.003	0.02	t [3]-0.03	0.007	1.33	0.33-2.00	0.511	0.11	0.09-0.12	0.009
1965-66	3 + 3	1.24	0.52-2.15	0.237							T [5]	n [4]-0.11	—						
Pa.																			
1969	3	1.48	0.92-2.61	0.563	0.05	0.04-0.07	0.010	(0.01) [2]	all t	(0.007)	0.14	0.03-0.35	0.105	1.00	0.33-1.67	0.387	0.08	0.06-0.10	0.012
1965-66	3 + 3	0.78	0.37-1.50	0.189							0.05	n-0.16	0.027						

TABLE 2.—*Fall residue[1] levels of DDE, DDT, DDD, dieldrin, PCBs, and mercury in pools of 25 wings of adult mallards or black ducks: 1969 compared with 1965-66* —Continued

State; year	No. of pools	Residues, in ppm (wet weight)																	
		DDE			DDT			DDD			Dieldrin			PCB's			Mercury		
		Mean	Extreme values	Std. error	Mean	Extreme values	Std. error	Mean	Extreme values	Std. error	Mean	Extreme values	Std. error	Mean	Extreme values	Std. error	Mean	Extreme values	Std. error
MALLARDS, ATLANTIC FLYWAY—Continued																			
N.J.																			
1969	3	2.62	2.38-2.86	0.240	0.22	0.17-0.26	0.045	0.05	0.05-0.05	0	0.07	0.05-0.09	0.020	5.94	0.18-11.7	5.76	0.11	0.10-0.12	0.010
1965-66	3 + 3	1.08	0.40-2.60	0.383							T	n-0.06	—						
Md.																			
1969	2	0.55	0.38-0.77	0.116	0.03	t-0.05	0.012	(0.01)	all t	(0.010)	(0.01)	t-0.02	(0.007)	0.62	0.20-1.33	0.357	0.08	0.08-0.08	0
1965-66	3 + 2	0.44	0.20-0.84	0.118							0.05	n-0.17	0.034						
Va.																			
1969	2	0.45	0.41-0.48	0.035	0.22	0.05-0.40	0.175	0.03	0.02-0.03	0.005	0.04	t-0.07	0.030	0.56	0.13-1.00	0.435	0.16	0.15-0.16	0.005
1965-66	3 + 3	0.30	0.19-0.59	0.061							0.06	n-0.11	0.018						
S.C.																			
1969	3	0.65	0.44-0.94	0.151	0.14	0.09-0.22	0.040	0.02	0.02-0.02	0	0.02	0.02-0.03	0.003	0.52	0.17-0.99	0.244	0.13	0.11-0.15	0.012
1965-66	3 + 3	0.37	0.13-1.00	0.133							0.05	n [4]-0.16	0.026						
Ga. & Fla.																			
1969	2	0.82	0.49-1.32	0.255	0.06	0.05-0.06	0.003	(0.01)[3]	t [2]-0.02	(0.010)	0.02	t-0.02	0.003	0.97	0.25-1.67	0.410	0.12	0.09-0.18	0.029
1965-66	2 + 2	0.53	0.35-0.70	0.079							n	—	—						
MALLARDS, MISSISSIPPI FLYWAY																			
Minn.																			
1969	5	0.30	0.20-0.42	0.040	0.04	0.02-0.08	0.010	T [5]	all t	—	(0.01)	all t	(0.004)	0.70	0.16-1.33	0.214	0.08	0.06-0.10	0.007
1965-66	7 + 6	0.24	0.08-0.52	0.039							n	—	—						
Wisc.																			
1969	5	0.34	0.19-0.48	0.055	0.03	0.02-0.05	0.005	T	all t	—	(0.01)	all t	(0.004)	0.58	0.17-1.00	0.179	0.26	0.05-1.00	0.184
1965-66	3 + 5	0.28	0.08-0.81	0.096							T	n-0.05	—						
Mich.																			
1969	3	0.45	0.33-0.53	0.061	0.05	0.02-0.08	0.018	T [5]	t [2]-0.02	—	0.03	0.02-0.05	0.010	0.62	t-1.00	0.302	0.11	0.08-0.14	0.017
1965-66	2 + 3	0.22	0.10-0.48	0.067							n [4]	—	—						
Iowa																			
1969	4	0.33	0.16-0.54	0.094	0.05	t-0.09	0.019	T	all t	—	0.03	0.02-0.05	0.006	0.13	0.07-0.25	0.041	0.08	0.06-0.10	0.009
1965-66	5 + 5	0.22	0.06-0.92	0.080							n	—	—						
Ill.																			
1969	6	0.73	0.18-2.69	0.395	0.12	0.02-0.54	0.085	0.05	t-0.26	0.043	0.04	0.02-0.07	0.008	0.36	0.13-1.00	0.131	0.06	0.05-0.08	0.005
1965-66	7 + 6	0.09	n-0.27	0.020							T	n-0.06	—						
Ind.																			
1969	1	0.19	—	—	0.02	—	—	T	—	—	0.03	—	—	1.00	—	—	0.06	—	—
1965-66	4 + 3	0.17	0.06-0.29	0.034							T	n-<0.05	—						
Ohio																			
1969	3	0.38	0.24-0.54	0.087	0.18	0.05-0.30	0.073	T	t-0.02	—	0.09	0.04-0.15	0.033	0.66	0.03-1.66	0.504	0.10	0.08-0.12	0.012
1965-66	3 + 3	0.24	0.15-0.31	0.028							n	—	—						
Mo.																			
1969	5	0.20	0.13-0.30	0.029	0.02	t [2]-0.04	0.007	T [5]	all t	—	0.05	0.04-0.06	0.004	0.21	0.10-0.33	0.052	0.07	0.05-0.11	0.012
1965-66	6 + 5	0.13	n-0.72	0.065							n [4]	—	—						
Ky.																			
1969	1	0.33	—	—	0.04	—	—	T	—	—	0.03	—	—	0.33	—	—	0.09	—	—
1965-66	3 + 3	0.30	0.13-0.62	0.080							n	—	—						
Ark.																			
1969	6	0.25	0.21-0.28	0.013	0.12	0.04-0.16	0.019	0.03	t-0.04	0.004	0.06	0.02-0.11	0.013	0.16	t-0.67	0.103	0.08	0.06-0.10	0.007
1965-66	7 + 6	0.20	0.08-0.31	0.021							0.08	n-0.34	0.028						
Tenn.																			
1969	4	0.26	0.20-0.34	0.029	0.06	0.02-0.11	0.023	T	all t	—	0.04	0.02-0.04	0.005	0.71	0.25-1.66	0.333	0.08	0.07-0.12	0.012
1965-66	5 + 4	0.33	0.11-1.10	0.099							0.06	n-0.39	0.043						

La.																			
1969	5	0.44	0.27-0.74	0.081	0.11	0.07-0.19	0.026	0.02	t-0.03	0.003	0.05	0.04-0.07	0.007	0.23	0.07-0.50	0.074	0.08	0.06-0.09	0.005
1965-66	5 + 6	0.18	0.05-0.26	0.018							T	n-0.05	—						
Miss.																			
1969	2	0.52	0.36-0.68	0.160	0.14	0.05-0.22	0.009	0.04	0.04-0.05	0.005	0.04	0.04-0.05	0.005	0.10	t [a]-0.17	0.075	0.08	0.07-0.08	0.005
1965-66	3 + 3	0.51	0.21-0.96	0.137							T [5]	n [4]-0.05	—						
Ala.																			
1969	1	1.75	—	—	0.09	—	—	2.07	—	—	0.09	—	—	0.42	—	—	0.06	—	—
1965-66	2 + 3	2.17	0.54-5.31	0.922							0.05	n-0.14	0.035						
MALLARDS, CENTRAL FLYWAY																			
Mont. (east)																			
1969	4	0.11	0.08-0.17	0.020	0.03	t-0.08	0.017	0.02	t-0.03	0.008	0.04	t-0.06	0.010	0.18	0.13-0.25	0.025	0.07	0.05-0.09	0.008
1965-66	8 + 4	0.09	0.05-0.16	0.010							T	n-0.16	—						
N. Dak.																			
1969	6	0.25	0.14-0.44	0.050	0.03	t-0.06	0.008	T	all t	—	(0.01) [2]	all t	(0.003)	0.13	t-0.50	0.076	0.08	0.06-0.11	0.008
1965-66	8 + 8	0.12	0.05-0.43	0.022							n	—	—						
S. Dak.																			
1969	6	0.09	0.07-0.14	0.011	(0.01)	t-0.02	(0.003)	T	n-t	—	(0.01)	all t	(0.003)	0.13	t-0.25	0.034	0.06	0.05-0.09	0.006
1965-66	7 + 8	0.11	n-0.20	0.014							n	—	—						
Wyo. (east)																			
1969	3	0.13	0.08-0.19	0.032	0.02	t [a]-0.03	0.009	T [5]	all t	—	0.02	t-0.02	0.003	0.30	0.25-0.33	0.027	0.08	0.07-0.09	0.006
1965-66	1 + 3	0.16	0.05-0.45	0.097							n [4]	—	—						
Nebr.																			
1969	7	0.13	0.06-0.19	0.017	(0.01) [2]	t-0.02	(0.003)	T	all t	—	(0.01)	t-0.02	(0.004)	0.06	t-0.13	0.015	0.09	0.07-0.13	0.010
1965-66	6 + 7	0.10	0.05-0.17	0.009							n	—	—						
Colo. (east)																			
1969	4	0.46	0.13-1.25	0.266	0.06	0.02-0.09	0.015	T	t-0.02	—	0.02	t-0.03	0.006	0.43	0.07-1.33	0.301	0.08	0.07-0.10	0.007
1965-66	10 + 4	0.30	0.17-0.85	0.048							n	—	—						
Kans.																			
1969	6	0.11	0.08-0.15	0.011	0.02	t-0.06	0.008	T	t-0.02	—	0.02	t-0.03	0.005	0.15	0.03-0.50	0.072	0.06	t-0.09	0.010
1965-66	7 + 6	0.08	n-0.12	0.009							n	—	—						
N.M. (east)																			
1969	3	0.37	0.26-0.57	0.099	0.03	0.02-0.05	0.009	T	all t	—	0.02	t-0.02	0.003	0.18	0.13-0.25	0.037	0.09	0.06-0.10	0.013
1965-66	3 + 3	0.74	0.22-2.44	0.349							T	n-0.06	—						
Okla.																			
1969	4	0.15	0.13-0.18	0.012	0.02	0.02-0.02	0	T [5]	t [a]-0.02	—	0.03	t-0.08	0.019	0.12	t-0.23	0.058	0.08	0.05-0.11	0.013
1965-66	5 + 4	0.11	0.07-0.20	0.016							n [4]	—	—						
Tex.																			
1969	6	0.98	0.13-4.38	0.683	0.09	t-0.38	0.059	T	t-0.02	—	0.07	t-0.26	0.039	0.20	t-0.67	0.100	0.06	0.05-0.07	0.003
1965-66	6 + 9	0.35	0.12-1.14	0.072							0.08	n-0.53	0.037						
MALLARDS, PACIFIC FLYWAY																			
Wash.																			
1969	8	0.36	0.19-0.48	0.037	0.04	0.03-0.05	0.003	T	t-0.02	—	(0.01) [2]	t-0.02	(0.004)	0.14	t-0.33	0.039	0.09	0.05-0.18	0.014
1965-66	13 + 11	0.47	0.06-2.75	0.125							T	n-0.10	—						
Oreg.																			
1969	7	0.48	0.21-1.03	0.122	0.09	0.03-0.29	0.037	T	t-0.03	—	0.03	t-0.12	0.017	0.10	t-0.20	0.020	0.09	0.06-0.10	0.006
1965-66	7 + 7	0.36	0.12-0.59	0.038							T	n-0.09	—						
Idaho																			
1969	8	0.48	0.23-0.79	0.069	0.08	0.05-0.22	0.021	T [5]	t [a]-0.02	—	0.02	t-0.05	0.006	0.14	0.10-0.32	0.028	0.10	0.08-0.15	0.009
1965-66	9 + 9	0.51	0.06-2.77	0.140							T	n [4]-0.09	—						
Mont. (west)																			
1969	4	0.14	0.07-0.21	0.029	0.03	t-0.05	0.009	T	all t	—	(0.01) [2]	all t	(0.005)	0.15	0.03-0.27	0.050	0.10	0.10-0.11	0.003
1965-66	4 + 4	0.17	0.08-0.34	0.031							T	n-0.06	—						
Wyo. (west)																			
1969	2	0.12	0.09-0.14	0.025	0.02	t-0.03	0.010	T	all t	—	0.02	t-0.03	0.010	0.12	0.10-0.13	0.015	0.12	0.10-0.13	0.015
1965-66	2 + 3	0.07	n-0.10	0.015							n	—	—						
Calif.																			
1969	8	1.52	0.99-2.70	0.190	0.19	0.09-0.37	0.035	0.04	t-0.22	0.026	0.02	t-0.10	0.012	0.04	t-0.10	0.013	0.08	0.05-0.11	0.007
1965-66	11 + 11	1.45	0.02-3.50	0.174							T	n-0.08	—						

TABLE 2.—*Fall residue[1] levels of DDE, DDT, DDD, dieldrin, PCBs, and mercury in pools of 25 wings of adult mallards or black ducks: 1969 compared with 1965-66* —Continued

State; year	No. of pools	Residues, in ppm (wet weight)																	
		DDE			DDT			DDD			Dieldrin			PCB's			Mercury		
		Mean	Extreme values	Std. error	Mean	Extreme values	Std. error	Mean	Extreme values	Std. error	Mean	Extreme values	Std. error	Mean	Extreme values	Std. error	Mean	Extreme values	Std. error
MALLARDS, PACIFIC FLYWAY—Continued																			
Nev.																			
1969	3	0.24	0.20-0.33	0.043	0.05	0.02-0.08	0.018	T	all t	—	0.02	t-0.05	0.014	0.73	t-1.66	0.487	0.37	0.23-0.55	0.095
1965-66	2 + 3	0.23	0.08-0.37	0.047							n	—	—						
Utah																			
1969	5	1.29	0.49-2.09	0.294	0.28	0.04-0.44	0.075	0.03	0.02-0.03	0.002	0.08	0.03-0.23	0.037	0.26	0.07-0.50	0.069	0.09	0.06-0.10	0.008
1965-66	6 + 5	0.93	0.39-1.41	0.102							0.05	n-0.16	0.019						
Colo. (west)																			
1969	3	0.36	0.19-0.63	0.137	0.05	0.02-0.08	0.018	T	all t	—	0.05	t-0.11	0.032	0.22	0.17-0.25	0.024	0.10	0.09-0.12	0.010
1965-66	3 + 3	0.69	0.11-3.20	0.504							n	—	—						
Ariz. & N.M. (west)																			
1969	3	0.68	0.25-1.52	0.418	0.02	t-0.03	0.006	T	t-0.02	—	(0.01)	all t	(0.007)	0.12	t-0.17	0.050	0.12	0.09-0.14	0.015
1965-66	1 + 3	0.31	n-0.73	0.146							0.05	n-0.12	0.030						

[1] Limits of residue quantification: DDE, DDT, DDD, or dieldrin = 0.02 ppm in 1969 and 0.05 ppm in 1965 and 1966; PCBs = 0.03 ppm, and mercury (metallic equivalent) = 0.05 ppm (1969 only). **CAUTION:** Do not compare 1969 DDT or DDD levels with 1965-66 readings; these readings may reflect PCB interference and have been deleted.

[2] Parenthesized values are approximations involving trace residues derived to develop flyway statistics where practicable. Means assume trace values equal one-half the limit of quantification; standard errors have been maximized.

[3] t: pool residues detected at levels below 1969 limit of quantification.

[4] n: residues not detectable at limit of quantification.

[5] T: mean residue level probably lower than limit of quantification.

TABLE 3.—*Mean residues[1] of DDE, DDT, DDD, and dieldrin, by waterfowl flyways, in pools of 25 wings of adult mallards or black ducks in 1969 and in 1965-66; and residues of PCB's and mercury in 1969*

Species	Flyway	Year	No. of pools	Residues, ppm (wet weight)											
				DDE		DDT		DDD		Dieldrin		PCB's		Mercury	
				Mean	Std. error	Mean	Std. error	Mean	Std. error	Mean	Std. error	Mean	Std. error	Mean	Std. error
Black Duck	Atlantic	1969	41	1.42	0.103	0.12	0.011	0.03	0.019	0.14	0.057	1.20	0.124	0.19	0.022
		1965-66	89	1.23	0.078					0.05	0.008	n.a.[2]		n.a.	
Mallard	Atlantic	1969	18	1.05	0.139	0.09	0.014	0.02	0.002	0.05	0.025	1.29	0.457	0.10	0.004
		1965-66	39	0.72	0.078					T[3]	—	n.a.		n.a.	
Mallard	Mississippi	1969	51	0.40	0.058	0.08	0.012	(0.05)[4]	—	0.04	0.003	0.35	0.044	0.09	0.014
		1965-66	123	0.25	0.024					T	—	n.a.		n.a.	
Mallard	Central	1969	49	0.30	0.098	0.03	0.009	T	—	0.02	0.006	0.17	0.039	0.08	0.003
		1965-66	117	0.17	0.017					T	—	n.a.		n.a.	
Mallard	Pacific	1969	51	0.71	0.054	0.11	0.012	T	—	0.02	0.005	0.13	0.014	0.10	0.004
		1965-66	117	0.70	0.063					T	—	n.a.		n.a.	

[1] See table 2 for limits of quantification and caution regarding DDT or DDD comparisons.
[2] n.a. = no analysis.
[3] T = mean residue level probably lower than limit of quantification.
[4] Parenthesized approximation involving trace residues.

TABLE 4.—*Pesticide residues in wings of individual adult mallards: California, 1969-70*

October 18-November 15, 1969								January 1-10, 1970						
			Residue, ppm (wet weight)								Residue, ppm (wet weight)			
County	Date	Sex	DDE	DDD	DDT	Dieldrin		County	Date	Sex	DDE	DDD	DDT	Dieldrin
NORTHEASTERN COUNTIES														
Modoc	Oct 18	M	0.13	t[1]	t	t								
Siskiyou	Oct 18	M	0.18	t	t	t								
Lassen	Oct 18	M	0.20	t	0.02	t								
Siskiyou	Oct 19	M	0.29	t	0.02	t								
Siskiyou	Oct 20	M	6.60	t	0.42	t								
Modoc	Oct 18	F	0.26	t	t	t								
Modoc	Oct 18	F	0.38	t	0.02	t		No January wings available						
Modoc	Oct 18	F	0.41	t	0.02	t								
Modoc	Oct 18	F	0.63	t	0.03	t								
Siskiyou	Oct 19	F	1.08	t	0.14	t								
	Median	M	0.20	t	0.02	t								
		F	0.41	t	0.02	t								
SACRAMENTO VALLEY COUNTIES														
Sutter	Oct 25	M	0.49	t	0.10	0.02		Glenn	Jan 7	M	0.18	t	0.02	t
Yolo	Oct 18	M	0.62	t	0.09	t		Yuba	Jan 3	M	0.25	t	0.03	t
Colusa	Oct 25	M	0.82	0.04	0.21	0.03		Colusa	Jan 8	M	0.28	t	0.02	t
Butte	Oct 19	M	1.21	0.02	0.20	t		Glenn	Jan 9	M	0.31	0.02	0.04	t
Sutter	Oct 25	M	3.47	0.04	0.18	0.02		Butte	Jan 3	M	0.44	t	0.12	0.03
Butte	Oct 19	M	4.86	t	0.22	t		Butte	Jan 10	M	0.45	0.02	0.08	t
Sutter	Oct 18	M	5.05	0.10	0.26	0.06		Colusa	Jan 4	M	0.48	t	0.05	t
Colusa	Oct 25	M	5.91	0.02	0.69	0.03		Glenn	Jan 7	M	0.70	t	0.06	0.03
Yolo	Oct 18	M	6.67	0.04	0.57	0.02		Colusa	Jan 7	M	1.48	0.04	0.06	t
Colusa	Oct 25	M	12.37	0.02	0.20	t		Yolo	Jan 9	M	1.62	0.02	0.33	t
Glenn	Oct 25	M	41.72	0.11	2.46	0.03		Butte	Jan 9	M	2.66	0.06	0.48	t
Sacramento	Oct 18	F	0.18	t	0.03	t		Colusa	Jan 7	M	7.13	0.05	0.40	0.02
Sutter	Oct 18	F	0.47	t	0.10	0.02		Placer	Jan 7	F	0.94	0.02	0.17	t
Colusa	Oct 25	F	1.45	0.03	0.55	0.03		Colusa	Jan 3	F	3.79	t	0.11	t
Colusa	Oct 25	F	1.73	t	0.14	0.02		Butte	Jan 7	F	4.67	0.41	0.72	0.03
	Median	M	4.86	t	0.22	t			Median	M	0.47	t	0.07	t
		F	0.96	0.02	0.33	0.03				F	3.79	t	0.11	t
SAN JOAQUIN VALLEY COUNTIES														
Fresno	Nov 9	M	0.32	t	0.09	0.03		Contra Costa	Jan 9	M	0.32	t	0.05	t
Fresno	Oct 22	M	0.58	0.02	0.07	0.02		Fresno	Jan 1	M	0.44	t	0.08	t
Fresno	Oct 18	M	0.66	0.02	0.15	t		Merced	Jan 3	M	0.60	t	0.05	t
San Joaquin	Oct 19	M	0.86	t	0.05	t		San Joaquin	Jan 9	M	4.58	t	0.11	t
Fresno	Nov 10	M	4.20	0.05	0.47	t		Fresno	Jan 1	M	30.65	0.51	6.65	0.11
Fresno	Oct 22	M	20.10	t	0.23	t		Merced	Jan 3	F	0.13	t	0.03	t
Merced	Oct 22	F	0.44	t	0.05	t		Merced	Jan 3	F	0.15	t	0.02	t
San Joaquin	Oct 19	F	1.24	0.05	0.97	0.02								
Merced	Oct 18	F	1.26	0.03	0.53	0.02								
Merced	Nov 15	F	1.49	t	0.07	t								
Fresno	Oct 19	F	1.51	0.04	0.39	0.02								
Fresno	Oct 19	F	1.78	0.02	0.17	0.12								
San Joaquin	Nov 8	F	2.02	0.03	0.58	0.02								
	Median	M	0.76	t	0.10	t			Median	M	0.60	t	0.05	t
		F	1.49	t	0.07	t				F	0.14	t	0.02	t

[1] t: residue detected at level below limit of quantification.

TABLE 5.—*Pesticide residues in wings of individual adult black ducks: New Jersey and New York, late 1969*

October 17-26, 1969							December 13-27, 1969						
			Residue, ppm (wet weight)							Residue, ppm (wet weight)			
County	Date	Sex	DDE	DDD	DDT	Dieldrin	County	Date	Sex	DDE	DDD	DDT	Dieldrin
NEW JERSEY: COASTAL AND DELAWARE BAY COUNTIES													
Cumberland	Oct 21	M	0.51	0.02	0.08	t [1]	Atlantic	Dec 22	M	0.36	0.02	0.05	0.02
Atlantic	Oct 25	M	0.86	0.02	0.13	t	Cumberland	Dec 13	M	0.75	0.02	0.09	0.02
Ocean	Oct 20	M	1.88	t	0.05	t	Cumberland	Oct 26	M	0.96	0.02	0.08	0.02
Bergen	Oct 18	M	3.04	0.06	0.26	0.07	Atlantic	Dec 23	M	1.30	0.02	0.14	t
Cumberland	Oct 18	M	3.19	0.02	0.39	t	Hudson	Dec 19	M	2.43	0.14	0.40	0.25
Cape May	Oct 23	M	4.74	0.15	0.48	0.02	Atlantic	Dec 20	M	3.44	0.03	0.36	0.03
Atlantic	Oct 23	M	6.00	0.04	0.46	0.03	Ocean	Dec 19	M	5.20	0.15	0.59	0.02
Atlantic	Oct 24	M	8.08	0.03	0.54	t							
Cape May	Oct 22	M	13.79	t	0.14	t							
Bergen	Oct 23	F	0.41	t	0.02	t	Bergen	Dec 23	F	0.41	0.04	0.10	0.08
Bergen	Oct 23	F	3.96	lost	0.70	0.82	Bergen	Dec 27	F	0.61	0.27	0.12	0.30
Ocean	Oct 23	Unk	0.17	t	0.03	t	Cumberland	Dec 27	Unk	0.74	0.02	0.10	0.03
Cape May	Oct 25	Unk	1.83	0.03	0.04	t	Cumberland	Dec 24	Unk	0.98	t	0.07	t
							Cumberland	Dec 27	Unk	1.28	0.02	0.10	0.03
							Cumberland	Dec 27	Unk	1.65	0.08	0.43	0.06
							Cape May	Dec 13	Unk	2.97	0.02	0.22	0.08
							Essex	Dec 26	Unk	4.11	0.02	0.23	0.04
	Median	M	3.19	0.02	0.39	t		Median	M	1.30	0.02	0.14	0.02
		F	2.19	—	0.36	0.41			F	0.51	0.16	0.11	0.19

(Closed: November 17-30, 1969)

October 17-26, 1969							November 17-30, 1969						
			Residue, ppm (wet weight)							Residue, ppm (wet weight)			
County	Date	Sex	DDE	DDD	DDT	Dieldrin	County	Date	Sex	DDE	DDD	DDT	Dieldrin
UPSTATE NEW YORK													
Wayne	Oct 25	M	0.14	t	t	t	Ontario	Nov 24	M	0.30	0.04	0.02	0.02
Delaware	Oct 18	M	0.15	t	t	t	Ontario	Nov 22	M	0.49	t	0.04	t
Monroe	Oct 24	M	0.20	t	t	t	Ontario	Nov 22	M	0.82	0.02	0.06	0.05
Schoharie	Oct 26	M	0.45	t	0.03	t	Niagara	Nov 22	M	1.07	0.06	0.24	0.05
Dutchess	Oct 18	M	0.75	0.02	0.03	0.02							
Erie	Oct 17	M	1.71	t	0.03	t	Cayuga	Nov 24	F	0.05	t	t	t
Orange	Oct 23	M	1.77	t	0.05	t	Ontario	Nov 20	F	0.06	t	t	t
Washington	Oct 21	M	2.20	t	0.02	t	St. Lawrence	Nov 30	F	0.16	t	0.04	0.02
							Wayne	Nov 23	F	0.16	t	t	t
Fulton	Oct 21	F	0.17	t	0.02	t	Ontario	Nov 23	F	0.18	t	0.02	t
Seneca	Oct 23	F	0.18	t	0.02	t	Chautaugua	Nov 30	F	0.73	0.02	0.05	0.05
Jefferson	Oct 18	F	0.42	t	0.02	0.02	Ontario	Nov 23	F	3.08	t	0.18	0.03
							Westchester	Nov 17	Unk	0.28	0.02	0.03	0.03
Jefferson	Oct 20	Unk	0.22	t	t	t		Median	M	0.66	0.03	0.05	0.035
	Median	M	0.60	t	0.025	t			F	0.16	t	0.02	t
		F	0.18	t	0.02	t							

November 17-30, 1969						
			Residue, ppm (wet weight)			
County	Date	Sex	DDE	DDD	DDT	Dieldrin
LONG ISLAND						
Nassau	Nov 29	M	1.18	0.02	0.43	0.03
Suffolk	Nov 24	M	1.48	0.03	0.38	0.02
Suffolk	Nov 25	M	3.19	0.03	0.58	0.02
Suffolk	Nov 20	M	3.24	0.08	1.11	0.04
Nassau	Nov 24	F	0.20	t	0.03	t
Nassau	Nov 22	F	0.27	t	0.02	t
Nassau	Nov 22	F	0.43	0.02	0.14	0.03
Nassau	Nov 25	F	0.80	0.02	0.16	0.02
Suffolk	Nov 22	Unk	0.46	0.02	0.08	0.06
Suffolk	Nov 22	Unk	3.87	0.04	0.85	0.02
	Median	M	2.34	0.03	0.48	0.02
		F	0.35	0.015	0.085	0.015

No December wings available

[1] t: residue detected at level below limit of quantification.

Organochlorine Insecticide Residues in Sediment and Fish Tissues, Ontario, Canada

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H. E. Braun,[1] and C. W. Douglas[4]

ABSTRACT

River and lake sediments and several species of fish were collected from four study areas in the Province of Ontario. These consisted of one agricultural, two mixed agricultural—recreational, and one recreational study area. Large volumes of DDT and dieldrin were used in the first area, small quantities were used in the mixed areas, and insignificant quantities were used in the recreational area. The agricultural and mixed areas were located on deep alluvial soils; the recreational area was located on bare-to-thinly-covered Precambrian rock. Residue levels in sediments were similar in all four areas, but slightly higher in the recreational area. The ratios of DDT to its metabolites, DDE and TDE, were similar in all areas in that the metabolites predominated over the parent DDT. Residues of DDT and dieldrin in fish tissues tended to depend on feeding habits, fat content, and age of the fish. Residues in the sediment (dry weight) were almost the same as residues found in the low-fat benthic invertebrate and plankton feeders.

Residues increased in the low-fat piscivores, were slightly higher in the high-fat feeders, and were highest in the high-fat piscivores. The concentration of DDT and dieldrin in the tissues and extractable fat and the actual quantity accumulated per fish increased as size and weight of any one species increased. The increase in total DDT or dieldrin concentration from lowest to highest tissue residues of all fish species was of the order of 100 to 500 times; the increase in body load was of the order of 10^3 to 10^4. Higher concentrations in fish tissue were correlated with the higher sediment levels of the Precambrian recreational area. Data demonstrate that the use of even minute quantities of persistent chlorinated hydrocarbons in rocky Precambrian watersheds has a profound effect on sediment and biota contaminants. Use on deep rich soils has a similar effect, but not in the same proportion to the quantity used.

Introduction

The persistent organochlorine insecticides have been used for insect control over the past 25 years in the Province of Ontario. In the early years, DDT was registered for a multiplicity of uses in agriculture and forestry. During the 1950's it was used extensively by growers of tobacco, vegetables, and fruit, and was virtually eliminated from use by producers of dairy animals and other livestock. As agricultural and forestry uses became more specific, private and municipal uses became more general; DDT was used in the protection of shade trees and ornamentals and the control of biting flies in urban and recreational areas. Aldrin and dieldrin had special properties for the control of soil-borne insects injurious to crop production. Aldrin was used in urban areas to protect lawns, and dieldrin was used in industry to protect fabrics and timber products.

The persistence of these three insecticides has been reviewed previously (*1*). A range of 4 to 30 years for DDT and 5 to 25 years for dieldrin has been quoted for 95% disappearance from agricultural soils in the temperate zone. Unfortunately, this persistence is greatly extended because DDT breaks down into two persistent metabolites, TDE and DDE, and dieldrin is derived from aldrin which can persist for 1 to 6 years (*1*).

Dieldrin and DDT are of very low solubility in water (0.25 to 1.0 ppm and 0.1 to 3.7 ppb, respectively) and are tenaciously held by soil particles; hence movement through soils is insignificant (*1*). Movement into the

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aquatic environment on soil transported by wind or water is well documented (*1, 2*). In the aquatic environment DDT is reductively dechlorinated to TDE (*3,4*), especially by coliform bacteria (*3, 5*). One study (*6*) reported that a similar conversion occurs in soils under anaerobic conditions although normal breakdown under aerobic conditions gives rise to considerable DDE (1).

River sediments containing DDT are reported (*7*) to give traces of DDT in water although these have been only 1/18,000 of the sediment levels. Absorption of DDT from water via the gills of fish has been reported (*8,9*) as high as 80 to 90% in the first 10 hours after application. The external mucous coating of fish was also found to concentrate DDT and aid absorption through skin. In addition to this direct absorption from water, accumulations by fish through the food chain are now well documented (*10*). An accumulation factor of 10,000 has been reported from water to fish, incorporating both direct absorption and food chain concentration. With this in mind, standards of 0.5 and 0.25 ppb have been suggested as maximum reasonable stream allowances (*11*).

In this study four areas were selected where different patterns of DDT and dieldrin use had occurred in a four-year study: 1968-71. Residues were measured in the sediments of streams and lakes and attempts were made to correlate this to accumulations in different fish species.

Study Areas

Four study areas were selected in southern Ontario. Three have soils derived from glacial deposits; the fourth is on the Canadian Shield (Precambrian).

Agricultural Area 1: This study area covered the whole of Norfolk County and parts of Elgin, Oxford, Brant, and Haldimand Counties (Fig. 1). The area is characterized by a flat topography and deep sandy loam soils. Flue-cured tobacco was the major cash crop of the area with an annual production of 90,000 acres; this represents about 95% of the tobacco acreage in the Province. About 80% of the DDT and 8 to 9% of the aldrin-dieldrin used in Ontario have been applied to this area (Table 1). It is served by many creeks and tributaries to Long Point Bay, Lake Erie.

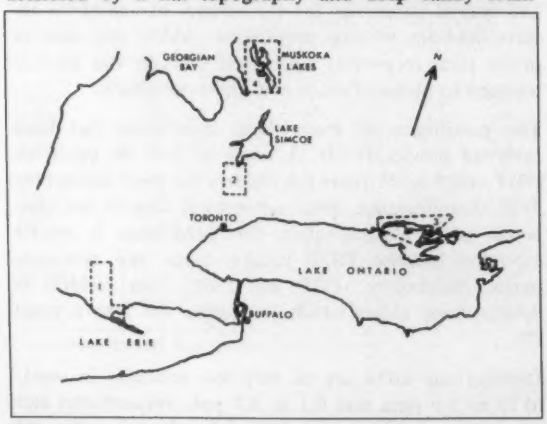

FIGURE 1.—*Areas sampled for organochlorine residues in Southern Ontario, 1968-71.*

Agricultural—Recreational Area 2: The area consists of an agricultural marsh with deep muck soils that drain into an adjacent lake. The area is located north of the city of Toronto and supplies that city with fresh vegetables. The marsh drains by way of the Holland-Schomberg River and tributaries to Lake Simcoe where the shoreline is developed for recreation and two sizable urban centers. In the past, DDT and aldrin-dieldrin were used intensively for vegetable production. The actual quantities of each were quite small (Table 1) but the rate of application per acre was high. DDT was used around the shoreline of Lake Simcoe to control biting flies.

Mixed Agricultural—Recreational Area 3: This is a relatively large area, situated on the north shore of Lake Ontario, devoted to low-intensity mixed agricultural—recreational pursuits with some urban development. Belleville is the largest city in the area. The topography is undulating and the soils vary from shallow to deep and sandy to clay loam. Agriculture is confined mainly to Prince Edward County and the lakeshore of Northumberland and Hastings. Much of the hinterland and lakeshore is recreational. Several rivers serve the area, including the Trent, Moira, Napanee, and Salmon. They drain into the Bay of Quinte before entering Lake Ontario. About 3 to 4% of the DDT used in the Province is used in this area for fruit and some vegetable production. Aldrin-dieldrin use was confined largely to potato and vegetable production. At least one factory on the river system used dieldrin; the purpose was to impregnate carpets.

Rcreational Area 4: The Muskoka lakes and rivers are popular recreational areas. This Precambrian area has little or no true soil and consists of lakes and rock outcrops with mixed deciduous and coniferous forest growing on shallow soils and detritus trapped between rocks. The whole system drains into the Georgian Bay and thence into Lake Huron. Use of DDT in this area was exceedingly small measured against use in the other areas, occurring mainly between the late 1950's and 1966 for the control of biting flies and for minor outbreaks of caterpillars and budworms.

Sediments were collected and fish were caught in gill nets from each of these four areas; samples were analyzed for DDT, its metabolites, dieldrin, and other organochlorine compounds.

TABLE 1.—*Quantities of DDT and aldrin/dieldrin used in four study areas, 1968-70*

Insecticide	Year	Agricultural Area 1 Total lb, %	Agricultural—Recreational Area 2 Total lb, %	Agricultural—Recreational Area 3 Total lb, %	Recreational [1] Area 4 Total lb	Total Use in Province, lb
DDT [2]	1968	246,000 (83)	14,100 (4.8)	13,000 (4.4)	None	296,300
	1969	365,000 (79)	14,400 (3.1)	13,800 (3.0)	None	463,100
	1970	154,500 (86)	5,330 (3.0)	5,100 (2.8)	None	179,500
Aldrin—Dieldrin [3]	1968	263,000 (8.1)	8,400	3,850	30	3,263,000
	1969	2,500 (9.3)	500	980	None	26,900
	1970	None	None	None	None	None

[1] Last recorded use in 1966.
[2] Based on analysis of 5 commercial formulations, content was 75.5% *p,p'*-DDT, 18.0% *o,p'*-DDT, 6.1% *p,p'*-TDE, and 0.4% DDE.
[3] Over 95% of the aldrin—dieldrin used as aldrin.

Analytical Procedures

Sediments were air dried, ground, and stored until analyzed. Mineral and organic sediments were analyzed differently. Mineral sediments (25 g) were brought to within 50% of field water storage capacity and left for 24 hours. Acetone and hexane in the ratio 1:1 (250 ml) were added to the sediment and the mixture was shaken for two hours. An aliquot (100 ml) was filtered off, water was added, and the organochlorine insecticides were partitioned into hexane. Organic sediments (25 g) were blended with acetonitrile and water (2:1) for 5 minutes and an aliquot (10 g) was filtered off. The filtrate was partitioned into hexane.

Fish were held in frozen storage at −20°C. A representative sample (10 g) of the eviscerated portion was mixed thoroughly with granular anhydrous sodium sulfate (100 g) and standard Ottawa sand (25 g) by grinding in a mortar and pestle until all tissue was finely subdivided and homogeneous. This mixture was transferred to a Soxhlet extraction apparatus and subjected to exhaustive extraction with hexane for 7 hours.

Extracts from sediments and fish tissues were evaporated to dryness by rotary vacuum at 45°C. In the case of fish the percentage of fat or oil was determined gravimetrically.

A one-step Florisil column cleanup method (*12*) was used for the isolation of organochlorine insecticides. Florisil (60-100 mesh) activated commercially at 650°C was reheated at 135°C for a minimum of 24 hours. After cooling, the adsorbent was partly deactivated by the addition of water at the rate of 5 ml/100 g and allowed to equilibrate.

Up to 1 g of fat from fish extracts and 10 g of sediment extract were mixed thoroughly with 25 g of conditioned Florisil. This was placed on top of a second 25-g portion of prewashed adsorbent in pyrex columns (25 mm by 300 mm) fitted with reservoirs (350 ml). The entire column was eluted with 300 ml of the 1:4 dichloromethane:hexane (v/v) solvent mixture at a percolation rate of approximately 5 ml per min. Eluates were concentrated just to dryness with rotary vacuum evaporation at 45°C, the residue was redissolved in 5 ml hexane and used for subsequent gas chromatographic analysis. All solvents employed were reagent grade chemicals which had been redistilled from glass.

Varian Aerograph Models 204 and 1200 gas chromatographs, equipped with 250 millicurie tritium electron capture detectors, were used for qualitative and quantitative assays. Operating parameters were as follows:

Column:	5 ft. by ⅛ in. Pyrex packed with 4% SE-30 + 6% QF-1 on Chromosorb W, preconditioned 72 hr. at 225°C (*13*).
Temperatures:	column, 175°C; detector, 200°C; injection block, 225°C.
Carrier gas:	N_2 at 40 ml/min.

Injection volumes of 5 μl were used for both sample solutions and comparison standards.

Qualitative residue confirmation was accomplished mainly with thin-layer chromatography (TLC) using silica gel. Plates were developed with 1% chloroform in *n*-heptane, and visualized with alkaline $AgNO_3$ spray as the chromogenic agent. Alternatively, *p,p'*-DDT and *p,p'*-TDE were confirmed by treatment with 5% methanolic KOH (*14*) to produce the corresponding dehydrochlorinated derivatives and reidentification by gas chromatography. Dieldrin levels in general were too low for confirmation by either TLC or chemical conversion. Partial confirmation of dieldrin was achieved by fractionating the analysis solution on the Mills column (*15*), thus isolating dieldrin in the second eluate fraction.

Percent recoveries of pesticides from fish tissue were checked periodically by fortification directly into the oil obtained as the result of the hexane extraction. Averaged recoveries were: *p,p'*-DDE, 97.8%; *o,p'*-DDT, 91.2%; *p,p'*-TDE, 94.6%; *p,p'*-DDT, 89.6%; dieldrin, 89.3%. The data presented in this report do not include corrections for percent recoveries. Polychlorinated biphenyls were isolated and measured separately in 1970 and 1971 and will be reported in a second paper. Separation was attempted in 1969 but difficulties were experienced. No separation was made in 1968. The number of samples collected in 1968 were few. Later analyses showed that from those study areas included in this paper PCB's represented no more than 5% of the gas-liquid chromatography responses to DDT and TDE and no more than 1% of the DDE.

Results

SEDIMENTS

A total of 314 sediments were analyzed from lakes and rivers in the four study areas. Residues of DDT, its metabolites, and dieldrin were measured in both the collective and drainage sections of each water system. Three of the study areas were situated on deep alluvial soils (areas 1, 2, and 3) and one was located on the rocky Canadian Shield (area 4). Waterways in the alluvial soils had sediment residues slightly below those on the shield (Tables 2 A,B,C,D). The range in mean ΣDDT for the total systems varied from 56 to 96 ppb in the three alluvial soil areas and 157 ppb on the shield. In the rivers of areas 1, 2, and 3, the range in mean ΣDDT was from 70 to 101 ppb, or about twice the residue found in the receiving bays or lakes where residues ranged from a mean ΣDDT of 26 to 56 ppb. In area 4, the collecting lake system had a mean residue of 170 ppb ΣDDT; the draining river averaged 110 ppb.

Area 1: The tobacco belt is situated on deep alluvial soil and its waterways vary from very sluggish (Dedrich Creek) to quite rapid. The mean ΣDDT in the river and creek sediments varied from 19 to 146 ppb and also varied greatly on a single waterway (Table 2A). Likewise, the mean dieldrin levels varied widely from nondetectable in several bodies of water to 2 ppb in Nanticoke Creek.

The highest sediment residues of DDT were in Big Creek (125 ppb) and Dedrich Creek (146 ppb), two watercourses that were either sluggish or associated with lands intensively planted in tobacco (Table 1). Statistically, these residues are significantly higher than those in the other rivers and creeks of this system. Residues of ΣDDT in the bay (29 ppb) were considerably lower than in the river system (95 ppb), suggesting dilution and/or degradation.

In most sediments *o,p'*-DDT as well as *p,p'*-DDT were found. In the formulation of DDT used in the area the ratio of these two ingredients was 4:1. In the creek sediments *p,p'*-DDT was 5 to 8 times the residue of *o,p'*-DDT; in the bay this had increased to 25 times.

In the creek sediments, the ratios of DDE:TDE:DDT, including *o,p'* and *p,p'*-DDT, were equal; in Long Point Bay, Lake Erie, however, the ratio was 2:8:1. The increase in DDT in the bay sediment would indicate considerable degradation in the bay. There was little difference in the composition of DDE, TDE, and DDT in six creeks and rivers in the system (Table 2A).

Area 2: Water courses in this mixed agricultural—recreational area were situated on a deep alluvial soil and were associated with a considerable area of muck soil. Most tributaries were sluggish and hence sediment texture and pesticide residues varied markedly from location to location. Sandy gravel sediments had a mean ΣDDT residue of 33 ppb and a mean dieldrin residue of 2.1 (Table 2B). Increases in residue levels appeared to be related to increased colloidal content. Organic silt had a mean ΣDDT of 170 ppb and a dieldrin residue of 3.2 ppb. The mean ΣDDT of the whole river system was 101 ppb ΣDDT and 7.8 ppb dieldrin.

In the lake sediments, which were largely sandy gravel, the mean ΣDDT was 56 ppb; no dieldrin could be detected. Movement of these two pesticides into Lake Simcoe appeared minimal as indicated by the absence of dieldrin.

Dieldrin, which was used largely for protection of vegetable crops on the marsh, appeared as residues in sediment in adjacent streams. The concentrations rose to a maximum of 137 ppb in localized sections of the river but was absent in seven Lake Simcoe sediments. DDT was used both for vegetable protection on the marsh and for controlling biting flies around the lake. Residues of DDT in the lake, therefore, were not indicative of downstream movement. When sandy gravel sediments from the rivers serving the marsh were compared with sediments of similar texture from the lake, residues of DDT and its metabolites were slightly higher in the lake sediments than in the river sediments (33 to 56 ppb). Since no clay silt or organic debris samples were collected from the lake, these could not be compared.

Some of the sediments from the river contained *o,p'*-DDT with the *p,p'*-DDT; however, lake sediments contained only *p,p'*-DDT. Although DDT was still being used in the marsh areas throughout the period of the study, its use around the lake was discontinued in 1966.

In the total river system the ratios of DDE:TDE:DDT, including *o,p'* and *p,p'*-DDT, were approximately 1:3:1, and in the lake, 1:3:5 (Table 2B). If sediments from the river are compared with those of similar texture from the lake, then ratios agree more closely. These ratios would indicate slower degradation in the sandy gravels than in the silts and organics, and suggest that lake residues were the result of local use rather than downstream movement. The most rapid degradation to TDE appeared to occur on the clay silt where ratios were 2:7:1.

Area 3: Rivers were located on shallow to deep alluvial soils and all drained into the Bay of Quinte in Lake Ontario. River sediments were quite sandy but contained considerable organic content. Mean ΣDDT residues in river sediments varied from 13 to 133 ppb with an average of 70 ppb (Table 2C). Each river showed considerable variation in residue from location to location. Mean dieldrin residues varied from 0.1 to 1.5 ppb and was 0.8 ppb for the total river system. The highest residues of DDT were found in sediment from the Trent River (133 ppb), a river associated with the

TABLE 2A.—*Residues or organochlorine insecticides in sediments from rivers and creeks in tobacco belt and Long Point B Lake Erie (Agricultural Area 1)*

Location		Number of Samples Analyzed	Content in dried sediment, ppb [1]					
			p,p'-DDE	*p,p'*-TDE	*o,p'*-DDT	*p,p'*-DDT	Total DDT	Dieldrin
1. River System								
Big Creek & Tributaries	—mean	79	46.5	40.1	7.4	31.1	125.1	0.7
	—max		560.0	300.0	2.95	1205.0	2360.0	140.0
	—min		ND	ND	ND	ND	ND	ND
Dedrich Creek	—mean	19	30.5	57.4	8.9	48.9	145.7	0.9
	—max		60.0	110.0	25.0	101.0	296.0	5.0
	—min		18.0	40.0	6.0	21.0	85.0	ND
Big & Little Otter Creeks	—mean	19	13.4	9.1	1.3	16.4	40.2	1.6
	—max		28.0	14.0	4.0	27.0	72.0	9.0
	—min		1.0	0.4	0.8	4.2	6.4	0.4
Nanticoke Creek	—mean	19	17.8	22.3	3.5	14.6	58.2	2.0
	—max		55.0	134.0	3.1	25.9	218.0	12.0
	—min		5.0	9.0	0.8	3.2	18.0	ND
Forestville Creek	—mean	3	6.7	6.7	ND	13.3	26.7	ND
	—max		20.0	20.0	ND	40.0	80.0	ND
	—min		ND	ND	ND	ND	ND	ND
Grand River	—mean	19	5.1	4.2	1.1	8.8	19.2	0.9
	—max		8.0	2.0	14.0	39.0	63.0	6.0
	—min		0.4	0.5	ND	0.3	1.2	0.4
Total River System [2]	—mean	158	31.4	31.4	5.5	26.5	94.8	1.0
2. Bay—Lake Erie								
Long Point Bay [3]	—mean	21	5.2	20.9	0.1	2.5	28.7	0.6
	—max		12.0	165.0	3.0	8.0	188.0	12.0
	—min		ND	ND	ND	ND	ND	ND
Total River—Bay System	—mean	179	28.3	30.1	4.8	23.7	86.9	1.0

[1] ND: not detected.
[2] ratio of DDE:TDE:DDT in river system was 1:1:1.
[3] ratio of DDE:TDE:DDT in Bay was 2:8:1.

TABLE 2B.—*Residues of organochlorine insecticides in sediment from Holland Schomberg River—Lake Simcoe System (Agricultural—Recreational Area 2)*

Location and Type of Sediment		Number of Samples Analyzed	Content in dried sediment, ppb [1]					
			p,p'-DDE	*p,p'*-TDE	*o,p'*-DDT	*p,p'*-DDT	Total DDT	Dieldrin
1. Holland Schomberg River [2]								
Sand—Gravel	—mean	11	5.8	12.5	2.2	12.5	33.0	2.1
	—max		19.0	42.0	17.0	63.0	141.0	12.0
	—min		2.0	1.0	ND	ND	3.0	ND
Clay—Silt	—mean	17	22.3	68.1	3.8	14.7	108.9	13.9
	—max		118.0	450.0	15.0	56.0	639.0	137.0
	—min		Trace	4.0	ND	ND	4.0	ND
Organic—Silt	—mean	9	33.3	119.4	ND	16.9	169.6	3.2
	—max		219.0	846.0	ND	104.0	1169.0	11.0
	—min		2.0	2.0	ND	5.0	9.0	ND
Total River System	—mean	37	20.1	63.8	2.4	14.6	100.9	7.8
2. Lake Simcoe [3]								
Sand—Gravel	—mean	7	5.7	16.1	ND	34.3	56.1	ND
	—max		25.0	70.0	Trace	173.0	268.0	ND
	—min		ND	ND	ND	ND	ND	ND
Total River—Lake System	—mean	44	17.8	56.2	2.0	17.8	93.8	6.6

[1] ND: not detected.
[2] ratio of DDE:TDE:DDT in river was 1:3:1.
[3] ratio of DDE:TDE:DDT in lake was 1:3:5.

greatest intensity of agricultural, industrial, and recreational pursuits. The Bay of Quinte contained sediments with a ΣDDT residue of 26 ppb, only one third those of the river system (70 ppb), but dieldrin residues (0.5 to 0.8 ppb) were almost as high as those of the river system.

Residues of TDE predominated in sediments of all rivers of this system, suggesting that breakdown occurred under anaerobic conditions. Residues in the Bay of Quinte were similar to those in sediments from all rivers: the metabolites DDE plus TDE to DDT had a ratio of 10:1 or greater (Table 2C). Measurable amounts of *o,p'*-DDT were found only in the Trent River, and were virtually absent from the river—bay system.

Area 4: Lakes Muskoka, Rosseau, and Joseph are contiguous bodies of water that are highly developed for recreation and are located on the Canadian Shield. Residues of DDT in the lake sediments varied from site to site; some were very low (3 ppb) and others were very high (1080 ppb). The mean ΣDDT residues for the three lakes, Muskoka, Rosseau, and Joseph, were 25, 250, 219, and 105 ppb, respectively (Table 2D). In Lake

TABLE 2C.—*Residues of organochlorine insecticides in sediments from Bay of Quinte, Lake Ontario, and rivers flowing into bay (Agricultural—Recreational Area 3)*

Location	Type of Sediment		Number of Samples Analyzed	Content in dried sediment, ppb [1]				
				p,p'-DDE	*p,p'*-TDE	*o,p'*- & *p,p'*-DDT [2]	Total DDT	Dieldrin
1. River System [3]								
Moira River	Organo-sand	—mean	6	13.7	24.5	3.5	41.7	1.0
		—max		9.0	123.0	ND	132.0	6.0
		—min		Trace	Trace	Trace	Trace	ND
Napanee River	Sandy-gravel	—mean	7	3.1	8.4	1.1	12.6	0.1
		—max		11.0	27.0	ND	38.0	1.0
		—min		Trace	Trace	Trace	Trace	Trace
Salmon River	Organo-sand	—mean	6	13.0	12.8	5.2	31.0	1.5
		—max		36.0	36.0	9.0	81.0	7.0
		—min		2.0	1.0	3.0	6.0	Trace
Trent River and Tributaries	Organo-sand	—mean	13	20.5	95.2	16.8	132.5	0.8
		—max		497.0	1160.0	109.0	1766.0	6.0
		—min		ND	ND	ND	ND	ND
Total River System		—mean	32	14.0	47.5	8.7	70.2	0.8
2. Bay—Lake Ontario [4]								
Bay of Quinte	Organo-silt	—mean	15	10.3	13.3	2.1	25.7	0.5
		—max		40.0	44.0	ND	84.0	2.0
		—min		2.0	1.0	2.0	5.0	ND
Total River—Bay System		—mean	47	12.8	36.6	6.6	56.0	0.7

[1] ND: not detected.
[2] *o,p'*-DDT was present only in sediment from Trent River where *o,p'*-DDT was 1.5 and *p,p'*-DDT 15.3 ppm.
[3] DDE:TDE:DDT ratio in river system was 2:6:1.
[4] DDE:TDE:DDT ratio in bay was 5:6:1.

TABLE 2D.—*Residues of organochlorine insecticides in sediment from Muskoka Lake System (Recreational Area 4)*

Location	Type of Sample		Number of Samples Analyzed	Content in dried sediment, ppb [1]				
				p,p'-DDE	*p,p'*-TDE	*p,p'*-DDT [2]	Total DDT	Dieldrin
1. Lake System [3]								
L. Muskoka	Fine & coarse sand	—mean	10	8	12	5	25	Trace
		—max		15	56	44	110	Trace
		—min		2	1	Trace	3	ND
	Clay silt	—mean	19	108	114	28	250	Trace
		—max		1080	1430	370	2880	Trace
		—min		2	1	Trace	3	ND
L. Rosseau	Clay & sand silt	—mean	5	91	112	16	219	ND
		—max		190	140	27	357	ND
		—min		10	30	2	42	ND
L. Joseph	Clay & sand silt	—mean	5	35	64	5	105	ND
		—max		130	230	25	385	ND
		—min		13	ND	ND	13	ND
Total Lake System		—mean	39	71	81	18	170	
2. River Outlet [4]								
Moon R.	Clay & sand silt	—mean	3	87	20	3	110	ND
		—max		150	30	5	185	ND
		—min		Trace	ND	ND	Trace	ND
N. Muskoka R.	Coarse sand	—mean	2	ND	ND	ND	ND	ND
Total Lake and River System		—mean	44	68	73	16	157	ND

[1] ND: not detected.
[2] *o,p'*-DDT not detected or in trace amounts.
[3] ratio of DDE:TDE:DDT in lake system 8:9:2.
[4] ratio of DDE:TDE:DDT in river outlet 27:7:1.

Muskoka there was a distinct difference in residue between sand and silt sediments. In 10 sandy sediments there was a mean residue of 25 ppb ΣDDT as opposed to 250 ppm for 19 silt sediments. In a traverse from shallow to deep water in the southern part of Lake Muskoka there were only slight differences in residues of sediments sampled at three depths. Sediments in the top inch contained 80 to 91 ppb ΣDDT; in the second inch the range was 13 to 36 ppb, and in the 2-4-inch depth it was 3 to 13 ppb. Residues were higher in the shallow water and declined only slightly in moderate and deep water.

The North Muskoka River which runs into the Muskoka Lakes had a coarse sand sediment in which DDT could not be detected. On the other hand, the Moon River which drains the three Muskoka Lakes into Georgian Bay, Lake Huron, had clay or silt sediments that contained a mean residue of 110 ppb ΣDDT. This river is also developed for recreation and, like the lakes, is surrounded by land that had been treated with DDT up to 1966. Since the amount of sediment moving down this river—lake system is considered very small, the largest quantity of DDT moving out of the area would be expected to be soluble. Movement of sediments later-

ally from shallow to deep water would be predicted to occur, but this would not remove residues from the system.

The ratio of DDE:TDE:DDT in the whole system indicated very low levels of the parent compound but higher residues of DDE and DDD. In the lakes this ratio was 8:9:2; in the outlet river the metabolite DDE increased to a ratio of 29:7:1 (Table 2D). Both ratios indicated considerably more breakdown of parent DDT to its metabolites than in any other system. Dieldrin and *o,p'*-DDT were virtually absent from the sediments of this system.

FISH SPECIES

A total of 1,926 sample analyses were conducted on 2,540 fish of 38 different species. In the four study areas: one agricultural, two agricultural—recreational, one recreational, there were multiple species of fish caught: 22, 20, 26, and 15, respectively. These species varied from low-fat benthic invertebrate and plankton feeders (less than 4%) to high-fat piscivores (over 7%). In each area certain species were caught predominantly in the lakes; other species were caught predominantly in rivers and streams. The following eight species were confined mainly to lake environments.

1. Alewife *(Alosa pseudoharengus)*
2. Burbot *(Lota lota)*
3. Cisco *(Coregonus artedii)*
4. Coho salmon *(Oncorhynchus kisutch)*
5. American smelt *(Osmerus mordax)*
6. Freshwater drum *(Aplodinotus grunniens)*
7. Lake Trout *(Salvelinus namaycush)*
8. Lake whitefish *(Coregonus clupeaformis)*

The following six species were caught mainly in the river environment:

1. Creek chub (*Semotilus atromaculatus*)
2. Blacknose dace (*Rhinichthys atratulus*)
3. Mooneye (*Hiodon tergisus*)
4. Brook trout (*Salvelinus fontinalis*)
5. Brown trout (*Salmo trutta*)
6. Rainbow trout (*Salmo gairdneri*)

All other species were caught in both rivers and lakes of one or more of the study areas.

The analysis data for both DDT and dieldrin are presented as tissue concentrations in the edible portion, as concentration in the extractable fat, and as total body loads of the whole fish (Tables 3, 4, 5).

Body loads are calculated from eviscerated fish concentrations and total body weights and are presented primarily for intraspecies comparison of residue accumulation with increasing size of fish. They cannot be combined as gross quantities of insecticide since the viscera may have concentrations quite different from muscle, nor should they be used for interspecies comparison because muscle weight to body weight ratios vary considerably between species. However, they can be used as a rough index of interspecies differences in pesticide accumulation which may reflect dietary preferences and habitat.

DDT—EDIBLE TISSUE CONCENTRATIONS

In only two study areas (areas 1, 3) were fish species found with mean ΣDDT levels below 0.1 ppm (Tables 3, 4). Of these, rockbass (*Ambloplites rupestris*), bluegill *(Lepomis macrochirus)*, and brown bullhead *(Ictalurus nebulosus)* were common to both areas, whereas yellow perch *(Perca flavescens)*, green sunfish (*Lepomis cyanellus*), and freshwater drum were present only in area 1, and pumpkinseed (*Lepomis gibbosus*) was present only in area 3. Most were of low fat content (less than 2%) and most belonged to the family Cypriniformes. Freshwater drum with a high fat content (7.3%) contained only 0.03 ppm ΣDDT and were caught in the outer bay at Long Point, Lake Erie.

More than half the species from all study areas contained residues of ΣDDT between 0.1 and 1.0 ppm. These included the majority of the low-, medium-, and high-fat plankton feeders, the low- to medium-fat bottom feeders, and the low-fat piscivores. Alewives from area 1 and blacknose dace and emerald shiners (*Notropis atherinoides*) from area 2 were present in this group, all with quite high fat content and low residues. Most of the bottom feeders were of low fat content (1-3%) and had mean residues between 0.1 and 0.3 ppm ΣDDT, although individual brown bullhead and channel catfish (*Ictalurus punctatus*) had residues up to 0.7 ppm.

Those piscivores which had residues between 0.1 and 1.0 ppm were largely low-fat species which devoured other low-fat species. These included northern pike (*Esox lucius*) and muskellunge (*Esox masquinongy*) from area 3, and burbot from all areas. These three fish species contained residues between 0.4 and 0.6 ppm ΣDDT and were from 1.0 to 2.9% fat. Walleye (*Stizostedion vitreum vitreum*) from area 3 also fell into this category; however, they averaged only 500 g and contained 1.2% fat and 0.3 ppm ΣDDT.

About 30% of the fish species had residues of ΣDDT between 1.0 and 10 ppm in the edible tissues. Included in this group were the high-fat bottom and plankton feeders and the medium-fat piscivores. In general, the benthos feeders had fat contents over 4% and contained less than 4 ppm ΣDDT. Plankton feeders with these high residues tended to have higher contents of fat and slightly lower ΣDDT residues. Alewives (area 1) and smelt in all areas fell into this group. Many of the low- to medium-fat piscivores had residues between 1.5 and 4 ppm ΣDDT. Largemouth bass (*Micropterus salmoides*), coho salmon, and brook, brown, and rainbow trout fell into this category.

TABLE 3.—*Fish species caught in 1968-71 in four study areas. 1: tobacco belt and Long Point Bay; 2: Holland—Schomberg Rivers and Lake Simcoe; 3: Bay of Quinte and its river system; 4: Muskoka Lake System*

Species	Area	Number of Fish Analyzed [1]	Average Weight, g	Fat, %	Content in edible tissue, ppm [2]				
					p,p'-DDE	*p,p'*-TDE	*p,p'*-DDT	Total DDT	Dieldrin
Clupeiformes									
Clupeidae									
Alewife	1	8	102	23.0	0.25	ND	ND	0.25	ND
(*Alosa pseudoharengus*)	3	10	53	15.6	0.64	0.16	0.53	1.33	0.042
Shad, Gizzard	3	11	310	3.3	0.184	0.148	0.094	0.426	0.009
(*Dorosoma cepedianum*)									
Cypriniformes									
Catostomidae									
Redhorse, Northern	1	3	742	1.52	0.062	0.037	0.063	0.162	0.009
(*Moxostoma macro-lepidotum*)	3	16	1,151	2.00	0.124	0.070	0.104	0.298	0.004
Sucker, Longnose	4	7	454	2.14	0.075	0.024	0.122	0.221	0.005
(*Catostomus catostomus*)									
Sucker, White	1	8	196	1.02	0.076	0.013	0.025	0.114	0.009
(*Catostomus commersoni*)	2	75	456	2.2	0.098	0.048	0.047	0.193	0.010
	3	55	581	1.42	0.049	0.046	0.093	0.188	0.003
	4	107	649	1.32	0.173	0.060	0.207	0.440	0.004
Cyprinidae									
Carp	1	2	1,519	4.9	0.140	0.080	0.030	0.250	0.023
(*Cyprinus carpio*)									
Chub, Creek	1	5	72	3.6	0.400	0.142	0.136	0.678	0.036
(*Semotilus atromaculatus*)	2	8	60	2.4	0.041	0.036	0.037	0.114	0.003
Dace, Blacknose	1	16	2.2	4.8	0.82	0.15	0.10	1.07	0.080
(*Rhinichthys atratulus*)	2	28	1.9	6.1	0.094	0.033	0.058	0.185	Trace
Shiners, Emerald	2	473 [1]	1.2	5.94	0.202	0.140	0.044	0.386	0.022
(*Notropis atherinoides*)									
Shiners, Golden	2	182 [1]	7.3	4.11	0.471	0.411	0.161	1.043	0.094
(*Notemigonus crysoleucas*)									
Shiners, Spottail	1	10	5.2	4.17	0.154	0.084	0.144	0.382	0.018
(*Notropis hudsonius*)									
Gadiformes									
Gadidae									
Burbot	2	22	1,952	1.0	0.196	0.062	0.105	0.363	0.004
(*Lota lota*)	4	9	903	1.4	0.097	0.046	0.209	0.352	0.006
Osteoglossiformes									
Hiodontidae									
Mooneye	3	6	242	3.3	0.079	0.033	0.039	0.151	0.007
(*Hiodon tergisus*)									
Perciformes									
Centrarchidae									
Bass, Largemouth	1	2	206	7.5	2.24	0.82	0.80	3.86	0.190
(*Micropterus salmoides*)	2	12	579	3.9	0.85	0.36	0.27	1.48	0.016
	3	4	380	1.0	0.060	0.023	0.041	0.124	0.001
Bass, rock	1	15	139	1.8	0.073	0.015	0.014	0.102	0.005
(*Ambloplites rupestris*)	2	21	130	2.4	0.142	0.069	0.088	0.299	0.012
	3	38	157	1.0	0.017	0.010	0.012	0.039	0.002
	4	70	175	0.8	0.096	0.034	0.121	0.251	0.005
Bass, Smallmouth	1	18	410	2.4	0.387	0.111	0.378	0.876	0.006
(*Micropterus dolomieui*)	2	36	552	6.0	0.85	0.32	0.45	1.62	0.021
	3	24	503	2.2	1.55	0.40	0.75	2.70	0.016
	4	34	266	2.2	0.28	0.15	0.64	1.07	0.024
Bluegill	1	6	200	1.5	0.12	0.010	0.011	0.033	0.002
(*Lepomis macrochirus*)	3	5	116	1.4	0.034	0.024	0.036	0.094	0.012
Crappie, Black	1	7	97	1.4	0.056	0.041	0.036	0.133	0.015
(*Pomoxis nigromaculatus*)	3	23	169	1.2	0.071	0.052	0.063	0.186	0.001
Pumpkinseed	1	12	94	3.1	0.133	0.077	0.088	0.298	0.015
(*Lepomis gibbosus*)	2	27	51	2.9	0.175	0.221	0.189	0.585	0.023
	3	47	108	1.4	0.014	0.008	0.010	0.032	0.001
	4	8	84	1.9	0.166	0.037	0.139	0.342	0.006
Sunfish, Green	1	4	199	2.3	0.050	ND	ND	0.050	ND
(*Lepomis cyanellus*)									
Cottidae									
Sculpin	2	22	7.5	4.2	0.022	0.044	0.040	0.106	0.004
(*Cottus* species)									
Percidae									
Perch, Yellow	1	14	122	1.6	0.057	0.010	0.020	0.087	0.002
(*Perca flavescens*)	2	48	171	2.4	0.279	0.097	0.119	0.495	0.015
	3	62	154	1.2	0.082	0.040	0.072	0.194	0.001
	4	36	131	0.8	0.143	0.045	0.188	0.376	0.005
Walleye	2	33	2,706	5.3	0.87	0.24	0.61	1.72	0.022
(*Stizostedion vitreum vitreum*)	3	72	500	1.4	0.109	0.53	0.108	0.270	0.003
	4	49	1,437	2.0	0.80	0.23	1.43	2.46	0.010
Sciaenidae									
Drum, Freshwater	1	10	239	7.3	0.033	ND	ND	0.033	ND
(*Aplodinotus grunniens*)									

TABLE 3.—*Fish species caught in 1968-71 in four study areas. 1: tobacco belt and Long Point Bay; 2: Holland—Schomberg Rivers and Lake Simcoe; 3: Bay of Quinte and its river system; 4: Muskoka Lake System*—Continued

Species	Area	Number of Fish Analyzed [1]	Average Weight, g	Fat, %	Content in edible tissue, ppm [2]				
					p,p'-DDE	*p,p'*-TDE	*p,p'*-DDT	Total DDT	Dieldrin
Serranidae									
Bass, White	1	12	123	3.2	0.093	0.003	0.019	0.115	0.003
(Roccus chrysops)	3	3	322	3.6	0.68	0.49	0.81	1.99	0.002
Perch, White	3	22	194	4.0	0.254	0.127	0.151	0.532	0.022
(Roccus americanus)									
Salmoniformes									
Esocidae									
Pike, Northern	2	14	993	2.9	0.307	0.104	0.157	0.568	0.006
(Esox lucius)	3	69	1,468	1.2	0.284	0.142	0.171	0.597	0.002
Muskellunge	3	1	1,939	2.4	0.304	0.115	0.166	0.585	0.007
(Esox masquinongy)	4	3	2,686	2.4	0.935	0.244	1.323	2.502	0.005
Osmeridae									
Smelt, American	1	13	25	2.2	0.039	0.038	0.087	0.164	0.011
(Osmerus mordax)	2	10	48	7.1	0.62	0.23	0.27	1.12	0.027
	3	7	36	8.6	1.28	0.75	1.20	3.23	0.043
	4	147	24	5.8	0.67	0.25	0.95	1.87	0.020
Salmonidae									
Cisco	2	9	101	11.2	0.32	0.29	0.67	1.28	0.046
(Coregonus artedii)	3	5	460	8.0	0.64	0.39	0.80	1.83	0.023
	4	6	453	5.2	1.03	0.53	2.68	4.24	0.014
Salmon, Coho	1	5	1,637	9.2	1.16	0.40	0.45	2.01	0.008
(Oncorhychus kisutch)	3	4	1,068	7.1	1.22	0.26	0.71	2.19	0.064
Trout, Brook	3	1	400	5.37	1.11	0.101	0.132	1.343	0.033
(Salvelinus fontinalis)	4	3	121	2.45	0.109	0.027	0.082	0.218	0.010
Trout, Lake	2	21	4,318	10.2	6.32	2.05	4.07	12.44	0.162
(Salvelinus namaycush)	3	1	286	3.59	0.632	0.505	0.182	1.319	0.026
	4	223	2,899	10.0	6.77	2.01	13.63	22.41	0.095
Trout, Brown	1	6	122	4.77	0.94	0.15	0.38	1.47	0.047
(Salmo trutta)	3	2	824	5.28	1.83	0.91	0.28	3.02	0.001
Trout, Rainbow	1	9	1,757	5.14	0.76	0.21	0.25	1.22	0.068
(Salmo gairdneri)									
Whitefish, Lake	2	21	687	4.3	0.48	0.27	0.74	1.49	0.004
(Coregonus clupeaformis)	3	4	1,549	15.3	0.88	0.68	0.88	2.44	0.254
	4	21	1,632	5.6	3.08	1.52	8.34	12.94	0.054
Siluriformes									
Ictaluridae									
Bullhead, Brown	1	6	169	1.6	0.026	0.015	0.013	0.054	0.002
(Ictalurus nebulosus)	2	5	100	2.4	0.280	0.170	0.059	0.515	0.047
	3	33	256	1.8	0.051	0.019	0.025	0.095	0.002
	4	13	280	1.7	0.296	0.092	0.187	0.575	0.005
Catfish, Channel	2	20	118	2.9	0.095	0.080	0.036	0.211	0.004
(Ictalurus punctatus)	3	2	2,515	12.7	0.310	0.233	0.127	0.680	0.027

[1] Analyzed in 20-sample analyses for each species.
[2] The overall ratios of DDE:TDE:DDT in fish were
Area 1 5:2:3
Area 2 9:5:6
Area 3 4:2:3
Area 4 6:2:9

Only two fish species contained residues over 10 ppm. These were lake trout, a piscivore caught in areas 2 and 4, and lake whitefish, a benthic invertebrate feeder caught in area 4. The lake trout contained about 10% fat and carried the highest residues of any fish: 12.4 ppm in area 2 and 22.4 ppm in area 4. Very high residues (12.9) in lake whitefish were recorded only from area 4; weight of these fish averaged 1600 g. The tissues of fish caught in the Muskoka Lakes had the highest residues of ΣDDT of all four areas; however, the average weight of fish from those lakes was greater than the average weight of fish from other waters. Data support the finding that a buildup of concentration in ΣDDT residues is related to increased fat content, which in itself reflects the feeding habits.

The ratio of DDE:TDE:DDT varied considerably between species and between locations; however, the general averages for all fish for areas 1, 2, and 3 were very similar. These ratios were approximately 5:2:3 in area 1, 9:5:6 in area 2, and 4:2:3 in area 3. Area 4 showed considerable difference from these; it had a ratio of 6:2:9, indicating a greater percentage of the parent compound and less breakdown to the two metabolites. These differences were reflected in most fish species to varying degrees. Of all species from the four areas, brown bullhead had the least variation in residue ratios.

DIELDRIN CONCENTRATIONS IN EDIBLE TISSUE

If the tissue residues of dieldrin are grouped into those fish containing (a) up to 0.010, (b) 0.011 to 0.100, and (c) over 0.101 ppm, then species are about equally divided into the first and second categories (Tables 3, 4).

TABLE 4.—*Fish species categorized 1968-71 according to level of total DDT and dieldrin in four study areas. 1: tobacco belt & Long Point Bay; 2: Holland—Schomberg Rivers & Lake Simcoe; 3: Bay of Quinte and its river system; 4: Muskoka Lake System*

Study Area	Insecticide	Residue in Edible Portion, ppm	Species
1	DDT, TDE, DDE	0.00-0.10	Bass R., Bluegill, Bullhead B., Perch Y., Sheepshead, and Sunfish G.
		0.11-1.0	Alewife, Bass S.M., Bass W., Carp, Chub C., Crappie B., Pumpkinseed, Redhorse N., Shiners S., Smelts A., and Sucker W.
2		1.1-10	Bass L.M., Dace B., Salmon C., Trout Brown, and Trout R.
		0.11-1.0	Bass R., Bullhead B., Burbot, Catfish C., Chub C., Dace B., Perch Y., Pike N., Pumpkinseed, Sculpin, Shiners E., Shiners G., and Sucker W.
		1.1-10	Bass L.M., Bass S.M., Cisco, Smelts A., Walleye, and Whitefish L.
		over 10	Trout L.
3		0.00-0.10	Bass R., Bluegill, Bullhead B., and Pumpkinseed.
		0.11-1.0	Bass L.M., Catfish C. Crappie B., Mooneye, Muskellunge, Perch W., Perch Y., Pike N., Redhorse N., Shad G., Sucker W., and Walleye.
		1.1-10	Alewife, Bass S.M., Bass W., Cisco, Salmon C., Smelts A., Trout Brook, Trout Brown, Trout L., and Whitefish L.
4		0.11-1.0	Bass R., Bullhead B., Burbot, Perch Y., Pumpkinseed, Sucker L.N., Sucker W., and Trout Brook.
		1.1-10	Bass S.M., Cisco, Muskellunge, Smelts A., and Walleye.
		over 10	Trout L., and Whitefish L.
1	Dieldrin	0.000-0.010	Alewife, Bass S., Bass S.M., Bass W., Bluegill, Bullhead B., Perch Y., Redhorse N., Salmon C., Sheepshead, Sucker W., and Sunfish G.
		0.011-0.100	Carp, Chub C., Crappie B., Dace B., Pumpkinseed, Shiners S., Smelts A., Trout Brook, Trout Brown, and Trout R.
		over 0.101	Bass L.M.
2		0.000-0.010	Burbot, Catfish C., Chub C., Dace B., Pike N., Sculpin, Sucker W., and Whitefish L.
		0.011-0.100	Bass L.M., Bass R., Bass S.M., Bullhead B., Cisco, Perch Y., Pumpkinseed, Shiners E., Shiners G., Smelts A., and Walleye.
		over 0.101	Trout L.
3		0.000-0.010	Bass L.M., Bass R., Bass W., Bullhead B., Crappie B., Mooneye, Muskellunge, Perch Y., Pike N., Pumpkinseed, Redhorse N., Shad G., Sucker W., Trout Brook, Trout Brown, and Walleye.
		0.011-0.100	Alewife, Bass S.M., Bluegill, Catfish C., Cisco, Perch W., Salmon C., Smelts A., and Trout L.
		over 0.101	Whitefish L.
4		0.000-0.010	Bass R., Bullhead B., Burbot, Muskellunge, Perch Y., Pumpkinseed, Sucker L.N., Sucker W., Trout Brook and Walleye.
		0.011-0.100	Bass S.M., Cisco, Smelts A., Trout L., and Whitefish L.

TABLE 5.—*Accumulations of DDT and its metabolites and dieldrin in several fish species by weight class at four study areas*

Species	Study Area	Weight Class, g	Number of Fish Analyzed	Average Weight, g	DDT and Metabolites in			Dieldrin in [1]		
					Tissue, ppm	Fat, ppm	Fish, µg	Tissue, ppm	Fat, ppm	Fish, µg
Cypriniformes										
Catostomidae										
Sucker, White	1	0- 300	7	124	0.12	15.1	15.0	0.007	0.89	1.60
(*Catostomus*		601- 900	1	699	0.08	2.4	55.9	ND	—	ND
commersoni)	2	0- 300	29	99	0.13	5.8	12.2	0.018	0.80	0.98
		301- 600	20	480	0.16	7.1	77.3	0.004	0.17	1.45
		601- 900	20	767	0.30	16.0	223.0	0.005	0.27	3.69
		901-1200	6	1,028	0.26	11.0	268.0	0.004	0.17	4.62
		over 1201	1	1,239	0.35	29.4	434.0	0.005	0.42	6.20
	3	0- 300	8	205	0.17	22.9	32.5	0.005	0.68	0.96
		301- 600	22	449	0.12	9.6	56.0	0.002	0.16	1.10
		601- 900	16	723	0.16	8.4	108.0	0.003	0.16	2.39
		901-1200	7	1,033	0.38	22.5	408.0	0.001	0.06	0.81
		over 1201	2	1,337	0.66	45.9	877.0	ND	—	—
	4	0- 300	20	225	0.09	13.7	17.1	0.002	0.32	0.56
		301- 600	27	428	0.15	13.5	70.0	0.004	0.35	1.59
		601- 900	20	746	0.98	52.9	743.0	0.004	0.22	3.20
		901-1200	30	1,022	0.55	37.7	560.0	0.006	0.41	5.64
		over 1201	10	1,349	0.50	29.5	658.0	0.007	0.42	8.82
Cyprinidae										
Shiners, Golden	2	0- 10	157	3.9	1.13	27.8	2.75	0.098	2.42	0.30
(*Notemigonus*		11- 20	17	12.0	0.69	13.7	8.24	0.065	1.28	0.77
crysoleucas)		21- 40	5	28.0	0.26	5.9	7.15	0.111	2.55	3.08
		over 101	3	109.0	0.04	4.5	4.64	0.035	3.64	3.85

TABLE 5.—*Accumulations of DDT and its metabolites and dieldrin in several fish species by weight class at four study areas* —Continued

Species	Study Area	Weight Class, g	Number of Fish Analyzed	Average Weight, g	DDT and Metabolites in			Dieldrin in [1]		
					Tissue, ppm	Fat, ppm	Fish, µg	Tissue, ppm	Fat, ppm	Fish, µg
Gadiformes										
Gadidae										
Burbot	2	0-1000	4	713	0.46	44.0	209.0	0.011	1.06	5.4
(Lota lota)		1001-2000	7	1,469	0.32	25.3	449.0	0.005	0.40	7.4
		2001-3000	9	2,565	0.36	47.1	454.0	0.006	0.78	14.4
		over 3001	2	3,363	0.32	59.4	1,063.0	0.005	0.94	16.8
	4	0-1000	7	769	0.34	21.2	264.0	0.005	0.31	3.6
		1001-2000	2	1,374	0.39	70.2	503.0	0.008	1.43	10.8
Perciformes										
Centrarchidae										
Bass, Largemouth	1	0- 300	2	153	3.86	51.5	740.0	0.190	4.92	34.9
(Micropterus	2	0- 300	5	206	0.95	25.4	201.0	0.005	0.13	1.04
salmoides)		301- 600	1	343	1.23	47.3	422.0	0.005	0.19	1.72
		601- 900	4	760	1.75	40.7	1,359.0	0.006	0.14	4.55
		over 901	2	1,264	2.36	62.9	2,603.0	0.067	1.79	103.0
	3	0- 300	2	245	0.02	1.8	4.8	0.001	0.09	0.20
		301- 600	2	515	0.23	25.5	119.0	ND	—	—
Bass, Rock										
(Ambloplites										
rupestris)	1	0- 100	7	79	0.18	8.3	12.7	0.016	0.73	1.02
		101- 200	8	149	0.47	17.8	62.2	0.016	0.61	1.79
	2	0- 100	6	60	0.28	9.1	16.2	0.022	0.72	1.68
		101- 200	13	145	0.30	13.6	37.3	0.008	0.36	1.11
		201- 300	2	248	0.21	13.1	49.2	0.007	0.43	1.95
	3	0- 100	6	77	0.04	2.8	2.9	0.002	0.16	0.14
		101 200	27	160	0.03	3.3	5.5	0.003	0.29	0.41
		201- 300	5	239	0.07	10.5	16.6	0.002	0.30	0.30
	4	0- 100	13	81	0.32	23.4	26.4	0.004	0.29	0.35
		101- 200	37	135	0.22	27.2	30.4	0.004	0.49	0.54
		201- 300	11	243	0.24	57.8	56.1	0.005	1.22	1.24
		over 301	9	390	0.27	52.5	110.0	0.007	1.35	2.76
Bass, Smallmouth										
(Micropterus										
dolomieui)	1	151- 300	10	213	0.51	32.9	109.0	0.004	0.26	0.75
		301- 450	4	352	0.88	47.5	310.0	0.006	0.32	2.11
		451- 600	2	469	2.41	81.7	1,113.0	0.020	0.68	9.02
		over 601	2	1,449	1.20	16.0	1,776.0	0.005	0.07	7.25
	2	0- 150	12	78	1.14	38.3	97.0	0.035	1.17	0.70
		151- 300	5	221	1.21	21.9	265.0	0.027	0.49	6.02
		301- 450	8	362	1.14	16.2	414.0	0.015	0.21	4.97
		451- 600	7	533	1.69	28.9	898.0	0.012	0.21	6.34
		over 601	12	959	1.86	29.9	1,761.0	0.013	0.21	11.76
	3	0- 150	4	101	0.13	7.8	11.0	0.003	0.18	0.38
		151- 300	4	229	0.10	6.5	25.0	0.001	0.06	0.33
		301- 450	7	344	0.22	13.1	77.0	0.002	0.12	0.76
		451- 600	3	525	0.33	25.2	115.0	0.003	0.23	1.73
		over 601	6	1,164	10.6	255.0	12,205.0	0.055	1.33	76.4
	4	0- 150	16	108	0.50	18.9	59.0	0.008	0.31	0.89
		151- 300	9	192	0.76	41.6	138.0	0.005	0.27	0.83
		451- 600	6	512	0.95	54.6	462.0	0.016	0.92	8.59
		over 601	3	834	4.43	258.0	5,507.0	0.181	1.05	164.0
Crappie, Black										
(Pomoxis										
nigromaculatus)	1	0- 150	6	84	0.13	8.4	11.1	0.017	1.12	1.04
		151- 300	1	173	0.17	17.9	29.4	0.006	0.63	1.04
	3	0- 150	15	106	0.10	12.0	8.30	0.002	0.25	0.09
		151- 300	4	204	0.03	3.1	6.21	0.002	0.20	0.43
		301- 450	4	371	0.65	21.3	272.0	—	—	—
Pumpkinseed										
(Lepomis gibbosus)	1	0- 50	3	33	1.28	27.0	39.0	0.033	0.70	4.85
		51- 100	4	81	0.08	3.1	6.0	0.017	0.68	1.33
		101- 150	4	117	0.05	1.6	5.7	0.004	0.14	0.42
		151- 200	1	174	0.05	2.2	8.7	Trace	0.02	0.07
	2	0- 50	13	29	0.94	28.8	27.0	0.036	1.10	0.94
		51- 100	13	67	0.21	8.1	14.9	0.010	0.39	0.66
		101- 150	1	107	0.76	30.6	81.0	0.010	0.40	1.09
	3	0- 50	2	20	0.07	2.7	1.2	0.001	0.04	0.01
		51- 100	11	90	0.03	2.5	1.9	0.001	0.08	0.08
		101- 150	33	118	0.03	2.4	3.3	0.001	0.08	0.12
		151- 200	1	156	0.04	2.1	6.4	0.006	0.03	0.94
	4	0- 50	2	47	0.24	26.8	11.5	0.013	1.43	0.61
		51- 100	2	61	0.28	14.1	16.2	0.006	0.30	0.34
		101- 150	4	113	0.42	17.5	47.9	0.008	0.33	0.87

TABLE 5.—*Accumulations of DDT and its metabolites and dieldrin in several fish species by weight class at four study areas* —Continued

Species	Study Area	Weight Class, G	Number of Fish Analyzed	Average Weight, G	DDT and Metabolites in			Dieldrin in [1]		
					Tissue, ppm	Fat, ppm	Fish, μG	Tissue, ppm	Fat, ppm	Fish, μG
Percidae										
Perch, Yellow	1	0- 100	2	89	0.05	3.9	4.8	0.005	0.43	0.40
(Perca flavescens)		101- 200	12	125	0.09	5.6	11.5	0.002	0.12	0.22
	2	0- 100	11	59	0.52	21.1	22.4	0.042	1.71	1.35
		101- 200	23	137	0.41	18.0	54.6	0.006	0.26	0.83
		201- 300	5	251	0.42	15.4	99.7	0.008	0.30	1.91
		over 301	9	364	0.66	23.1	239.0	0.009	0.31	3.41
	3	0- 100	13	60	0.14	12.0	8.8	0.001	0.09	0.10
		101- 200	36	148	0.20	16.8	30.8	0.002	0.17	0.22
		201- 300	12	254	0.25	22.4	60.5	0.001	0.09	0.15
		over 301	1	372	0.14	9.2	52.8	Trace	0.03	0.04
	4	0- 100	11	84	0.21	26.6	17.2	0.003	0.38	0.21
		101- 200	23	139	0.38	50.0	54.0	0.005	0.66	0.77
		201- 300	1	230	0.87	74.2	200.0	0.009	0.77	2.07
		over 301	1	360	1.69	235.0	608.0	0.017	2.36	6.12
Walleye										
(Stizostedion vitreum vitreum)	2	0-1000	9	605	0.32	6.8	209.0	0.016	0.34	9.0
		1001-2000	7	1,476	0.68	11.2	994.0	0.019	0.31	28.0
		2001-3000	5	2,386	4.03	64.5	9,860.0	0.025	0.40	59.1
		3001-4000	5	3,529	2.59	51.9	8,993.0	0.025	0.50	86.0
		over 4001	7	6,280	2.04	43.7	13,290.0	0.026	0.56	154.0
	3	0-1000	65	418	0.24	18.3	104.0	0.003	0.23	1.3
		1001-2000	6	1,206	0.20	9.7	240.0	0.004	0.19	4.8
		2001-3000	1	2,300	2.77	112.0	6,371.0	0.001	0.04	2.3
	4	0-1000	26	332	0.80	72.9	352.0	0.007	0.64	3.3
		1001-2000	10	1,409	2.32	104.0	3,012.0	0.014	0.63	18.5
		2001-3000	5	2,424	3.01	124.0	5,743.0	0.018	0.74	45.3
		3001-4000	3	3,337	3.05	98.4	10,140.0	0.026	0.83	93.6
		over 4001	5	4,902	10.4	193.0	50,140.0	0.030	0.56	144.0
Serranidae										
Perch, White	3	0- 150	7	116	0.36	8.6	55.6	0.028	0.68	3.12
(Roccus americanus)		151- 300	13	204	0.66	15.3	131.0	0.024	0.56	4.40
		301- 450	2	397	0.35	27.3	136.0	0.001	0.08	0.40
Salmoniformes										
Esocidae										
Pike, Northern	2	0-1000	2	625	0.09	5.8	68.0	0.002	0.14	0.61
(Esox lucius)		1001-2000	9	1,566	0.45	14.5	702.0	0.006	0.19	7.81
		2001-3000	1	2,782	0.850	26.6	2,365.0	0.010	0.31	2.8
		over 3001	2	4,887	1.43	51.1	6,932.0	0.008	0.29	38.0
	3	0-1000	25	569	0.22	28.6	125.0	0.001	0.13	0.38
		1001-2000	30	1,467	0.75	50.1	1,122.0	0.004	0.27	4.91
		2001-3000	7	2,286	0.73	52.9	1,723.0	0.001	0.07	3.19
		over 3001	7	3,869	0.86	63.5	3,910.0	0.005	0.37	21.0
Osmeridae										
Smelt, American	1	0- 20	4	16	0.13	7.4	2.0	0.009	0.52	0.14
(Osmerus mordax)		21- 40	9	28	0.19	8.0	5.3	0.013	0.55	0.34
	2	21- 40	4	30	0.61	11.3	18.4	0.015	0.28	0.46
		41- 60	2	50	1.79	19.5	92.7	0.050	0.54	2.41
		61- 80	4	66	1.29	15.5	846.0	0.033	0.40	1.80
	3	0- 20	1	16	2.14	23.7	33.6	0.062	0.69	0.97
		21- 40	4	31	2.81	34.6	85.1	0.040	0.49	1.27
		41- 60	2	54	4.62	57.3	243.0	0.041	0.51	2.26
	4	0- 20	113	17	2.00	29.5	34.2	0.023	0.34	0.39
		21- 40	25	25	1.69	32.6	43.8	0.025	0.48	0.64
		41- 60	6	54	1.19	38.6	51.7	0.008	0.27	0.44
		61- 80	3	66	1.23	37.6	82.3	0.013	0.40	0.89
Salmonidae										
Cisco	2	0- 200	9	101	0.13	1.2	130.0	0.046	0.41	4.6
(Coregonus artedii)	3	201- 400	2	327	0.48	9.7	152.0	0.015	0.30	4.9
		401- 600	3	548	1.02	10.3	562.0	0.028	0.28	15.5
	4	201- 400	17	314	3.43	52.9	1,074.0	0.015	0.24	4.9
		401- 600	39	485	4.27	63.4	2,126.0	0.014	0.21	6.7
		over 601	5	730	6.21	107.0	4,543.0	0.028	0.48	21.1
Trout, Lake & Brook										
(Salvelinus namaycush & Salvelinus fontinalis)	2	0-2000	2	1,252	4.61	50.0	7,371.0	0.095	1.03	158.0
		2001-4000	7	3,230	11.1	112.0	35,520.0	0.147	1.48	460.0
		4001-6000	7	4,570	17.6	174.0	83,420.0	0.203	2.01	908.0
		6001-8000	4	6,562	9.72	85.0	62,700.0	0.158	1.38	1,034.0
	3	0-2000	2 [2]	343	1.3	30.0	457.0	0.030	0.67	10.1
	4	0-2000	67 [2]	761	15.3	282.0	9,394.0	0.034	0.63	53.0
		2001-4000	108	2,785	24.1	211.0	67,570.0	0.109	0.79	333.0
		4001-6000	32	4,605	29.2	228.0	139,200.0	0.108	0.84	506.0
		6001-8000	12	6,644	40.5	413.0	272,300.0	0.109	1.11	733.0
		over 8001	8	8,731	65.8	419.0	570,600.0	0.228	1.53	1,994.0

TABLE 5.—*Accumulations of DDT and its metabolites and dieldrin in several fish species by weight class at four study areas* —Continued

Species	Study Area	Weight Class, g	Number of Fish Analyzed	Average Weight, g	DDT and Metabolites in			Dieldrin in [1]		
					Tissue, ppm	Fat, ppm	Fish, μg	Tissue, ppm	Fat, ppm	Fish, μg
Trout, Brown & Rainbow										
(Salmo trutta & Salmo gairdneri)	1	0-1000	10	182	1.45	31.4	192.0	0.048	1.04	6.7
		1001-2000	2	1,415	1.08	18.1	1,518.0	0.100	1.68	137.0
		2001-3000	2	2,750	1.03	18.3	2,828.0	0.070	1.24	193.0
		over 3001	1	6,400	1.35	25.1	8,640.0	0.070	1.30	448.0
	3	0-1000	2	824	3.02	57.2	226.0	0.001	0.02	0.8
Whitefish, Lake	2	0- 700	10	493	0.87	23.1	486.0	0.008	0.21	4.0
(Coregonus clupeaformis)		701-1400	11	762	2.18	44.9	2,000.0	0.006	0.12	4.8
	3	701-1400	3	1,238	2.36	14.8	2,921.0	0.274	1.72	341.0
		over 2101	1	2,483	2.68	20.2	6,662.0	0.193	1.45	479.0
	4	0- 700	3	566	9.49	348.0	5,758.0	0.044	1.61	23.9
		701-1400	5	1,108	16.6	327.0	17,460.0	0.050	0.98	61.6
		1401-2100	6	1,636	16.3	260.0	18,780.0	0.069	1.10	99.3
		over 2101	7	2,460	12.1	185.0	31,730.0	0.044	0.67	119.0
Siluriformes										
Ictaluridae										
Bullhead, Brown	1	0- 150	1	95.0	0.10	7.9	0.9	0.004	0.33	0.04
(Ictalurus nebulosus)		151-300	3	167.0	0.03	2.9	5.9	0.002	0.18	0.35
		301- 450	2	360.0	0.07	2.1	23.2	Trace	0.02	0.14
	2	0- 150	3	47.0	0.37	11.7	13.9	0.059	1.86	2.27
		151- 300	2	179.0	0.71	59.4	132.0	0.030	2.50	5.46
	3	0- 150	4	114.0	0.06	2.3	6.5	0.004	0.15	0.31
		151- 300	16	216.0	0.04	2.2	8.2	0.002	0.11	0.46
		301- 450	13	349.0	0.17	10.5	64.2	0.001	0.06	0.36
	4	0- 150	2	114.0	0.48	73.7	54.6	0.007	1.08	0.80
		151- 300	7	227.0	0.34	19.1	77.4	0.004	0.22	0.90
		301- 450	2	341.0	0.85	35.7	290.0	0.008	0.34	2.90
		over 451	2	568.0	1.21	68.8	704.0	0.005	0.28	3.16
Catfish, Channel										
(Ictalurus punctatus)	2	0- 100	9	90	0.18	6.9	15.9	0.003	0.11	0.31
		101- 200	10	133	0.23	7.3	32.5	0.008	0.26	0.68
		201- 300	1	233	0.33	10.5	76.0	0.002	0.06	0.47

[1] ND: not detected.
[2] One brook & one lake trout.
[3] Three brook & 64 lake trout.

Fish with residues below 0.010 ppm were mainly bottom feeders or plankton feeders; there were also a few low-fat piscivores such as pike, muskellunge, and walleye. In areas 3 and 4 the majority of fish species fell into this low-fat category.

The fish with tissue residues between 0.011 and 0.100 ppm dieldrin included fish with higher fat content, such as the benthic invertebrate, plankton feeders, and piscivores. The majority of the feeders had residues below 0.05; the piscivores trout and salmon were above this level. The majority of fish species caught in areas 1 and 2 had residues in this middle range.

Only three species, one in each of the first three study areas, had residues over 0.1 ppm; these ranged from 0.19 to 0.26 ppm. The three species were largemouth bass in area 1, lake trout in area 2, and lake whitefish in area 3.

DDT—WEIGHT CLASSES

When fish species were divided into weight classes, a general trend of increasing tissue concentrations and increasing body loads of ΣDDT could be correlated with the increasing body weights (Table 5). This increase was not consistent for all areas or all species, but the trend was evident. In some cases, however, increasing body weights were accompanied by decreasing tissue concentrations and either increasing body loads, e.g., pumpkinseed, or decreasing body loads, e.g., golden shiner (*Notemigonus crysoleucas*). When each weight class was well represented, the increases in both tissue concentrations and body load were readily observed; this was very evident with the fatty piscivores. Lake trout exhibited the greatest accumulations of ΣDDT.

Among the centrarchids, pumpkinseed were placed in 50-g, rockbass in 100-g, smallmouth bass (*Micropterus dolomieui*) and black crappie (*Pomoxis nigromaculatus*) in 150-g, and largemouth bass in 300-g weight classes. In area 1 the lightest pumpkinseed had the highest body loads, tissue, and fat concentrations of ΣDDT. Subsequent growth appears to have been more rapid than the accumulations of ΣDDT; there was a noticeable decline in actual extractable fat from the smaller to the larger fish where this trend existed. In areas 2, 3, and 4 this species did exhibit a general increase in body burden of ΣDDT with increasing body weight. The heaviest class contained 81 μg of ΣDDT per 107 g of fish from area 2.

Rock bass, smallmouth bass, and black crappie all exhibited little or no increase in tissue concentrations, slight increase in the extractable fat, and marked in-

crease in the body burden of ΣDDT. The largest rockbass (mean 390 g) contained 0.27 ppm in the tissue, 52.5 ppm in the fat, and 110 μg in the whole fish. The highest residues in smallmouth bass were from area 3 where fish with a mean weight of 1,164 g averaged 10.6 ppm ΣDDT in the tissue, 255 ppm in the fat, and 12 mg in the body.

Largemouth bass contained increasing quantities of ΣDDT in both tissues and in the total fish body. Fish weighing 1,264 g from area 2 contained 2.4 ppm in the tissue, 64 ppm in the fat, and 2.6 mg as a body load.

Among the centrarchids, rockbass, black crappie, and pumpkinseed accumulated relatively low residues compared to the largemouth and smallmouth bass. These differences were probably related to feeding habits: the two species of bass become increasingly piscivorous and consume larger fish as they themselves increase in body weight, thus accumulating high residues.

Among the bottom feeding catostomids and ictalurids, channel catfish was placed in 100-g, brown bullhead grouped in 150-g, and white sucker (*Catostomus commersoni*) in 300-g weight classes. The general trend in all three species was for slight increases of ΣDDT in fat, tissue, and body burdens. Some inconsistencies occurred, but these were probably due to the inadequate sample size of the classes. The largest sample among these species was white sucker, and even when fish averaged 1,337 g in area 3, the body accumulation was only 0.9 mg ΣDDT, much less than in the piscivorous centrarchids. Based on two of these three species, areas 3 and 4 appeared to have the greater accumulations of ΣDDT in fish tissue.

Among the percids and serranids, yellow perch was placed in 100-g, white perch (*Roccus americanus*) in 150-g, and walleye in 1-kg weight classes. Yellow perch, which was present in all four areas, exhibited the general trend of increasing ΣDDT concentrations in tissue, fat, and fish body with increasing body weight. The largest class, caught in area 4, weighed 360 g and contained 1.69 ppm ΣDDT in the tissue, 235 ppm in fat, and 0.6 mg in the fish body. Residues in these perch indicated a greater accumulation in area 4 than in the other three areas. White perch were obtained in only one area but the same general trend was observed.

Walleye were caught in three of the four study areas and in all cases the same trend of increasing tissue and fat concentration and body load occurred. The largest class weighed 4.9 kg and contained 10.4 ppm ΣDDT in the tissue, 193 ppm in the fat, and had a body load of 50 mg per fish. The difference between perch and walleye was very obvious, based on size and ΣDDT accumulations.

Burbot, a low-fat piscivore, was placed in a 1-kg weight class. It was present in areas similar to those nurturing walleye but failed to accumulate tissue residues or body loads to the same extent. A general increase did occur with the increasing body weight, however. The low-fat northern pike showed a trend similar to walleye. Among these three piscivores accumulations may reflect the species of fish consumed, as all are voracious predators and all are relatively low fat species.

The smelt, a species related to the salmonids, was placed in a 20-g weight class. It showed a marked increase in tissue and fat concentrations and body loads as the body weight increased. Smelts averaging 66 g from area 2 accumulated up to 0.8 mg ΣDDT per fish.

Among the salmonids, the benthos feeders, cisco, and whitefish were placed in 200-g and 700-g weight classes; the predaceous trout were placed in 1-kg and 2-kg classes. In all classes a marked increase in tissue and fat concentrations and in body load of ΣDDT occurred with increasing body weight. Among the ciscoes the largest fish weighed 730 g and accumulated 4.5 mg per fish in area 4; these showed greater accumulations of DDT than did ciscoes from area 3. Among the whitefish, the largest fish (2.5 kg) were found in area 4; these contained residues of almost 32 mg ΣDDT per fish. This body burden was also greater than that for fish of similar size from area 3. Among fish of the lower weight classes, whitefish had greater accumulations than fish of similar size from area 2. Brown and rainbow trout from areas 1 and 3 weighing 6.4 kg accumulated up to 8.6 mg ΣDDT. Lake trout, a fish that attained the greatest size and contained the highest fat level, exhibited the greatest increases in tissue and fat concentrations and showed the highest body burdens. Almost 0.6 g ΣDDT was found in fish weighing 8.7 kg from area 4. These voracious predators were the peak of the food chain in areas 2 and 4. Compared to the smallest yellow perch and rockbass, they had up to 500 times as much ΣDDT in tissue and fat concentrations, and up to 1000 times as much in body burden.

TISSUE, FAT, AND BODY LOADS—DIELDRIN

Dieldrin residues were several magnitudes less than the ΣDDT, but nevertheless appeared to be present in all species. Tissue and fat concentrations were not readily correlated with body weight in most benthic invertebrate and plankton feeders but were more evident in the piscivores.

Findings generally showed a correlation between increased tissue concentration and body loads with increased body weight; this was not marked in those fish of low fat content, but became more evident in high-fat bottom and plankton feeders and low-fat piscivores, and was most evident in the high-fat piscivores.

Viewed by study area, concentrations in fish tissue were greatest in area 4, even when similar weight classes were compared. Comparing weight classes, fish species in area 4 that had markedly elevated ΣDDT residues were cisco, lake whitefish, lake trout, and walleye, with slight increases in yellow perch and white suckers. In area 1, the fish species which exhibited slightly higher residues were rockbass and smallmouth bass. In area 2, pumpkinseed and bullhead had residues that were slightly higher than in fish from other areas. In area 3, only smelts had residues that exceeded those in the other three areas. Since all weight classes are not fully represented, it is difficult to predict how weight classes would have compared at all levels.

Discussion

In spite of the fact that the volume of DDT and dieldrin used in the four study areas was quite different, residues in sediment from all four areas were similar. Characteristics of each area and placement of DDT and dieldrin probably had a marked effect on these findings. In areas 2, 3, and 4, DDT was used to control biting flies and was applied close to or over water, causing fairly direct contamination of both fish and sediments. Similar results of direct application have been observed in many bodies of water (*10*). In area 4 the contamination of water and sediment following use was facilitated by the absence of soil, or by the very thin cover of soil in the forested areas treated. In area 1, where DDT was used in large volume, a deep sandy loam soil likely prevented direct runoff into the aquatic environment, and transportation of DDT and dieldrin in this area by physical soil movement was probably greater than in any other area studied.

The parent material *o,p'*-DDT was detected only in sediments where DDT had been used recently: namely, the tobacco belt, the rivers of area 2, and the Trent River of area 3. On the other hand, *o,p'*-DDT was absent where DDT had not been used for several years: namely, the lake in area 2, most of area 3, and area 4.

The degradation pattern of DDT primarily to TDE and in lesser degree to DDE appeared similar in all four areas, in spite of the fact that DDT was still being used in areas 1, 2, and 3 during this study but had not been used since 1966 in area 4. These ratios were 22:78; 21:79; 12:88; and 10:90%, respectively. In areas 1 and 4 the ratio of the two metabolites DDE:TDE was 1:1, probably because sediments were more aerobic than those in areas 2 and 3 (1:3 and 1:4). This supposition is supported by studies of several authors (3, 5, 6), who demonstrated increased breakdown to DDE under aerobic conditions. In areas 1, 2, and 3 DDT was applied up to and including the years of this sampling program; yet the actual level of residues in the sediments were lower than in area 4. It could be predicted from these data that residues will take much longer to disappear from area 4 than from areas 1, 2, and 3. This slow disappearance and/or dispersion in the cooler, precambrian lake environment is in keeping with the findings of Brown and Brown (*16*) in a subarctic environment.

Hindin et al. (*7*) reported traces of DDT in water coming from sediments in the ratio of 1:18,000. In a continuing study in preparation on area 1, the authors found a ratio of 1:2,400 between water and sediment for total DDT, and 1:2,700 for dieldrin. The difference between these two sets of data could be explained by differences in actual residues in the sediment and differences in the characteristics of the body of water. Nevertheless, sediments act as reservoirs of organochlorine insecticides which are constantly available for incorporation into tissues of bottom living organisms. Although two studies (*8,9*) have demonstrated that fish can remove 80 to 90% of the DDT from water by gills, a third study (*17*) has shown that 10 times more DDT was accumulated from the food chain than directly from water during the period of observation. Sediment residues can therefore be either ingested directly by invertebrates or bottom feeders or indirectly by transfer through the water phase.

In this study the ratio of metabolites to DDT in a pooled average of all fish by area was 7:3 in areas 1, 2, and 3, and 9:11 in area 4. The first three areas were almost identical and could be closely correlated with that ratio in the sediment; however, area 4 was distinctly different both with respect to fish and sediment. These differences may be related to the limnological characteristics of this deep, oligotrophic lake system which varies markedly from the shallow, eutrophic conditions prevalent in the other areas. Ratios of the metabolites DDE and TDE in fish from the four areas were 2:1 in areas 1, 2, and 3; and 3:1 in area 4. These ratios are almost the reverse of those found in sediments.

Comparing the mean pesticide concentration by area, a multiplication factor from the lowest to the highest residue in fish ranged from 100 to 450. If weight class were taken into consideration, residue or magnification of the tissue from smallest to largest fish regardless of species varied from 130 to 530. If the body load of DDT in micrograms per fish is considered, an increase from the lowest to the highest ranged from 10^3 to 33 x 10^3. Dieldrin residues in tissue by a similar comparison rose by factors of 60 to 200. When weight class was included, the total accumulation per fish increased by multiples of 3 to 5 x 10^3.

The concentration of both DDT and dieldrin in sediment (dry-weight basis) was about equivalent to the residue found in the tissue of the lowest fish species. The mean residues of ΣDDT in sediment and fish with the lowest tissue concentrations for the four areas were: area

1: (agricultural): 0.07 and 0.03 ppm; areas 2 and 3 (agricultural—recreational): 0.09 and 0.04 ppm, and 0.06 and 0.02 ppm, respectively; area 4 (recreational): 0.16 and 0.22 ppm.

The relationships established in this study for ΣDDT between sediment and fish, with further data on water, provided a ratio of sediment to water of 2,400:1; the ratio of sediment to low-fat fish was about 1:1. The ratio of lowest fish to highest fish was between 10^3 and 10^4, which gives a ratio of water to highest piscivores of $1:10^6$ or 10^7. A similar ratio could also be applied to the accumulation of dieldrin residues.

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Relations of the Brown Pelican to Certain Environmental Pollutants [1]

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ABSTRACT

Nearly all brown pelican eggs collected from 13 colonies in South Carolina, Florida, and California in 1969 and from 17 colonies in South Carolina and Florida in 1970 exhibited eggshell thinning. Of the 100 eggs analyzed for residues of pollutants, all eggs contained measurable quantities of DDE; most eggs contained measurable quantities of p,p'-DDD, p,p'-DDT, dieldrin, or PCB's (polychlorinated biphenyls). All eggs contained measurable quantities of mercury. DDE appears to have been responsible for virtually all the eggshell thinning. There is strong evidence that DDE played a major role in lowered reproductive success in South Carolina and California, and this pollutant appears to be intimately related to the population decline in South Carolina. Other pollutants, particularly dieldrin, may have had deleterious effect on reproductive success in South Carolina. Carcasses of pelicans collected by shooting in Florida and South Carolina in 1970 varied in residue load according to age and geographic location. Birds under 1 year of age contained smaller quantities of residues than did birds 1 year or older.

Introduction

The brown pelican (*Pelecanus occidentalis*) has experienced drastic population declines in much of its range in the United States. The first indication of population decline was noted in the early 1960's when the large breeding population of the eastern brown pelican (*P. o. carolinensis*) in Louisiana was extirpated (*1*). In South Carolina, the population declined from over 5,000 breeding pairs to approximately 1,000 pairs by the late 1960's (*2, 3*). In California, near total reproductive failure has occurred in the California brown pelican (*P. o. californicus*) during the past several years (*4, 5*). The population in Florida has remained relatively stable over the past 5 years (*6, 7;* also: L. J. Williams, personal communication). The agent or agents responsible for the disappearance of the Louisiana population remain unknown, but the catastrophe in Cailfornia has been attributed to the DDT group of insecticides, particularly DDE (*4, 8, 9, 10*).

The objectives of this study are (a) to determine the relation of certain environmental pollutants to population trends of the eastern brown pelican in Florida and South Carolina, and (b) to examine the relation of these pollutants to reproductive success in South Carolina. Additional residue data are included from the California brown pelican. Eggs and birds from which residue data were determined and herein reported were collected in 1969 and 1970.

Sampling Procedures

Brown pelican eggs were collected in 1969 from one colony in California (10 eggs), two colonies in South Carolina (49 eggs), and ten colonies in Florida (81 eggs). The eggshell measurements of the eggs collected in 1969 from the southeastern colonies were reported previously (*3*); and some of the residue data for the eggs from California were previously reported (*11*). In 1970, an additional 186 eggs were collected: 146 from 15 colonies in Florida and 40 from two colonies in South Carolina (Fig. 1). The eggs were wrapped in aluminum foil and frozen within several days of collection. Shell thickness (shell and shell membranes) was measured at three sites on the waist with a micrometer graduated in units of 0.01 mm. The thoroughly dried shells were weighed to the nearest 0.0001 g.

When feasible, one egg was taken from each of 10 nests in each Florida colony; at least 20 were collected from each South Carolina colony. Except for a few instances in 1969, eggs were collected from nests that had no young; eggs in all stages of incubation, both fresh and

[1] U.S. Department of the Interior, Bureau of Sport Fisheries and Wildlife, Patuxent Wildlife Research Center, Laurel, Maryland 20810.

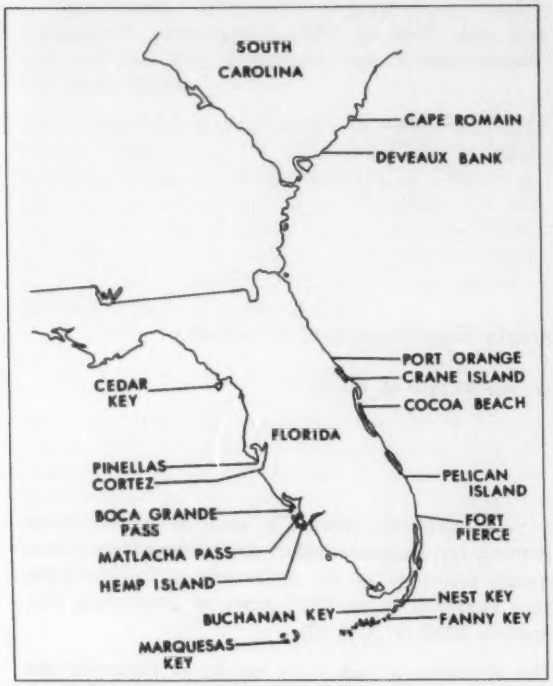

FIGURE 1.—*Colony sites where brown pelican eggs were collected in 1970.*

addled, were collected. In 1969, the eggs were collected in late May or early June except in the Deveaux Bank colony where they were collected in late July. In 1970, eggs were collected in February in three Florida Bay colonies; other colonies were visited in late April or early May. An attempt was made to sample as wide a segment of each colony as possible. The South Carolina colonies contain ground-nesting birds with only a few nests in low shrubs; this facilitated uniform sampling of the colony. It was more difficult to obtain a uniform sample in some Florida colonies because the pelicans nest in mangroves and other trees.

Pelicans were shot in three areas in Florida and in one area in South Carolina in 1970. Birds were collected in early June in Florida Bay and from July 7 to July 23 in the other areas. Pelicans were selected to represent a varied sample of age and sex. In one instance, a sick individual was collected; all other pelicans appeared normal.

In South Carolina, reproductive success was determined by directly counting or estimating the total number of nests and the total number of young fledged from those nests. Nests were counted on Marsh Island in 1969 and 1970 and on Deveaux Bank in 1970. The number of fledged young in each year was estimated as was the count of nests on Deveaux Bank in 1969.

Chemical Analyses

Eggs were analyzed individually for residues of organochlorine pesticides and their metabolites, polychlorinated biphenyls (PCB's), and mercury. The content of each egg was homogenized in a mixer; a 20-g aliquot was removed for pesticide and PCB analysis. A 5-g aliquot was removed for mercury analysis from each egg collected from South Carolina in 1970. The 20-g aliquots were ground with anhydrous sodium sulfate and extracted for 7 hours with hexane in a Soxhlet apparatus. Extracts were cleaned up by acetonitrile partitioning, and half were saved for PCB analysis. For insecticide analysis, residues in the cleaned extract were separated and removed in four fractions from a silica gel thin-layer plate (*12*). Each sample fraction was analyzed by electron capture gas chromatography on columns consisting of either a 3% OV-1 on Chromosorb W H. P. on 80/100 P, a 3% OV-17 on Gas Chrom Q on 100/120, or a 3.8% UCW-98 on Chrom W H.P. 80/100. DDT and metabolites in Fractions III or IV were confirmed on a column of 3% XE-60 or 3% QF-1 on Gas Chrom Q 60/80. PCB residues were identified and measured semi-quantitatively by a method involving thin-layer chromatography (*13*). The average recovery of the chlorinated insecticides and their metabolites from fortified eagle tissue ranged form 75 to 112%.

The California eggs, after freeze-drying, were analyzed for lead and total mercury by PPB, Incorporated, Columbia, Missouri (now defunct). The lead analysis was done on an atomic absorption spectrometer; a tantalum boat technique was used to increase sensitivity. The 1969 eggs from Florida and South Carolina were analyzed for total mercury by PPB, Incorporated, and Gulf General Atomic, Incorporated; quantification and identification of mercury in the freeze-dried eggs were made by multichannel gamma ray spectrometry. The analysis for mercury for the Florida Bay eggs and the analysis for lead in eggs not from California were conducted by the Environmental Trace Substances Center, Columbia, Missouri.

The mercury analysis of the 10 eggs collected in South Carolina in 1970 was for total mercury by a method developed by R. S. Christensen of the WARF Institute, Inc., Madison, Wisconsin (personal communication). The procedure involves acid digestion of the tissue and extraction of the mercury from the liquid digest with dithizone (*14*). Mercury determination was made on the dithizone extract by flame atomic absorption spectrophotometry using a sampling boat technique (*15*). The average recovery from tissue samples fortified with both inorganic mercury compounds was 91%.

The organochlorine residues of the pelican carcasses (body minus skin, head, feet, and gastrointestinal tract)

collected in 1970 and the eggs collected from Florida Bay in 1970 were analyzed by a method different from the procedure used for the other 80 eggs. Use of this method permitted analysis for mirex, which was not feasible using the method described above. The usual Soxhlet extraction with hexane was made on a 10-g aliquot of pelican carcass. An aliquot containing ≤0.4 g lipid was cleaned up by column chromatrography using the following procedure: Florisil, previously washed and recalcined at 1250°F according to the method of Hall (*16*), was partly deactivated with water (1-1.5%) to allow dieldrin to elute with the other pesticides and PCB's. A 19-mm-inside-diameter column containing 21 g of the treated Florisil topped with ½ in. sodium sulfate was prewashed with 50 ml hexane; the sample was added to the column and eluted with 200 ml of 6% ethyl ether in hexane. The Florisil eluate was evaporated to 20 ml and a 5-ml aliquot was transferred to a silicic acid column.

The reagents and apparatus used for the silicic acid column procedure were those specified by Armour and Burke (*17*) but modifications were made in collecting the eluants. The petroleum ether eluate was collected in two separate fractions of 100 and 300 ml, followed by 200 ml of the polar eluate (1% acetonitrile, 19% hexane, and 80% methylene chloride). The three fractions were concentrated and analyzed by gas chromotography (GC).

Using this procedure, mirex was collected in the first 100 ml of petroleum ether eluate. PCB's and DDE were collected in the second fraction; a previous study (*18*) showed that PCB preparations (Aroclor 1248, 1254, or 1260 as reference) do not interfere in the quantitative determination of DDE unless the ratio of PCB to DDE exceeds 10:1. The third fraction contained the rest of the pesticides.

Each fraction was analyzed on a Hewlett Packard 5750 gas chromatograph using a column of 4% SE-30/6% QF-1 on Supelcoport 100/120. Pesticides were quantitated by peak height; PCB's were estimated by comparing the total GC peak heights of PCB's in samples with that of Aroclor 1254. Recoveries from eagle tissue spiked with the organochlorine pesticides and 1254 ranged from 90 to 109%. The polar eluate of some samples was zoned by thin-layer chromatography (*12*) and run on a 3% SP 2401 column to confirm certain pesticide residues. PCB residues in most samples were confirmed by the thin-layer method of Mulhern et al. (*13*).

The minimum measurable quantity was 0.05 μg/g for most pesticides. The pelican egg residue measurements were not corrected for recovery values. Residues are expressed on a fresh wet-weight basis. We found that certain external egg measurements (length by breadth) were significantly correlated ($P<0.01$) with the weight of the contents of fresh eggs (*1*). The resulting regression equation was used to convert weight of the contents of all eggs to a fresh wet-weight basis (*19*). For purposes of comparison with other research, the contents of freshly laid brown pelican eggs contained an average of 84% moisture (determined by lyophilization) and 4.4% lipids. The percentage lipids remained essentially uniform until the embryo reached late development. At this stage (two-thirds or more development) the contents (adjusted to fresh wet weight) contained an average of 3.1% lipids, a significant drop ($P<0.01$; Student's *t*-test) from that found in the fresh egg. Romanoff (*20*) found a decrease of one-third of the lipid content of the hen's egg from laying to hatching.

A trace value for the pesticides or their metabolites, lead, or mercury was considered to be <0.1 μg/g, and a trace value for the PCB's was considered to be <1.0 μg/g. In order to quantify trace values and zero values (no residue detected) for statistical tests, the mean of these values was considered to lie halfway between the level of sensitivity and zero; each of these values was assigned this mean. Statistical analyses of the egg data were performed after logarithmic transformation of the residues. Residues in the 20 eggs collected from colonies in Florida Bay were not used in any of the statistical analysis except to show the mean and median for each colony.

Results and Discussion

RESIDUES

Measurable residues of *p,p'*-DDE were found in the 100 eggs analyzed; residues of *p,p'*-DDD, *p,p'*-DDT, dieldrin, and PCB's exceeded trace values in most eggs (Table 1). Measurable quantities of mercury were found in the 80 eggs analyzed for this metal. There was a great deal of variability in the DDE residues: California eggs (1969) had a geometric mean of 71 μg/g; residues in South Carolina eggs (Cape Romain) varied from 4.45 μg/g in 1969 to 2.83 in 1970; and residues in eggs from the Florida colonies (1969) averaged 0.69 to 2.48 μg/g DDE. Residues of DDE in eggs collected in 1969 from four geographic areas: Florida Gulf Coast, Florida Atlantic Coast, South Carolina, and California, were significantly different ($P<0.05$) from one another (Table 2). California eggs contained significantly more DDE and DDT than the eggs from the other areas; South Carolina eggs contained significantly more dieldrin. The highest levels of DDD and PCB's were also found in the South Carolina eggs; these residues were significantly higher than in the other areas except California. Excluding mercury, the lowest residues were found in the Florida Gulf Coast eggs. The lowest level of dieldrin was found in the California eggs, and the lowest level of mercury was found in the South Carolina eggs. The DDE:PCB ratio varied from 0.3:1 in the Marquesas Key Colony to 20:1 in the Anacapa Colony. All Anacapa eggs contained small residues

of *o,p'*-DDT and *o,p'*-DDD; it is extremely rare to find these isomers in tissues of vertebrates (*11*). Lead residues in the eggs were small; maximum residue was 0.17 μg/g. Most egg residues were usually positively intercorrelated ($P<0.05$) (Table 3). The exception was mercury which was negatively correlated with most of the other residues. The negative correlations probably occur as a result of a dissimilar pattern of mercury contamination from the organochlorines. The buildup of mercury in the food chain is likely to be of a different nature and of a lower magnitude than that associated with the organochlorines because most of the major forms of mercury in the ecosystem apparently are not lipid soluble. There were some differences between States in the correlations between egg residues.

The positive relationships between DDE and the other organochlorines were usually significant. To a lesser extent, this was also true of DDD and the PCB's. In contrast, the relationship of DDT to the other organochlorine residues, although positive, was usually not significant. The exception was in the California series where there was a significant positive relationship between DDT and DDE and between DDT and DDD. In the South Carolina eggs, the negative relationships between mercury and several of the organochlorines were significant. Although the full meaning of the relationship between residues is not clear, it is known that DDT is metabolized in the hen's egg to some extent (*21*). Consequently, there may be a breakdown from DDT to DDD in eggs containing dead embryos since this metabolism occurs in avian tissue after death (*22*). Thus the relationships in Table 3 may not necessarily be representative of those found in freshly laid eggs. However, it seems certain that the biological magnification of certain organochlorines (*p,p'*-DDE, *p,p'*-DDD, dieldrin, and PCB's) resembles a group effect in the pelican egg. That is, organochlorine residues tend to increase or decrease together, although the level of change for each chemical may be of a different magnitude.

Residue data are included for only one pelican found dead in the field (Table 4). This particular bird was observed in tremors on May 8 in the yard of a house located on Plantation Key, Florida. It was found dead on May 9. The cause of death is not known because no indications of serious disease or unduly high residues of pollutants were found. A hemolytic *Staphylococcus* was isolated from the heart blood, but the significance of this isolation was not determined. The carcass contained an array of residues, but these were lower than some of the residues from carcasses of pelicans collected in 1970 (Table 5). The residues in the brain were lower than those considered to be indicative of death from dieldrin (*23*), or from DDT or metabolites (*24, 25*).
Residues in the carcasses of birds collected in 1970 were quite variable, but all carcasses contained measurable residues of DDE and all contained at least a trace of PCB's (Table 5). The birds represented a wide range of age and both sexes; thus it would have little meaning to calculate the geometric mean or determine the median residue. The immature birds (1 to 2 years of age) and adult birds (3 years and older) always carried higher residues than did the young of the year. The age at which the brown pelican attains adult plumage is not definitely known; the age brackets for immature and adults pelicans are approximate. There was an indication that residues increased with age in young of the year, but this was not universally true.

Eggshell thicknesses of eggs from Florida Bay were near normal, and residues of DDE in these eggs averaged near 1 μg/g, which was generally lower than averages found in eggs from other colonies. Residues were much lower in adult and immature pelicans from Florida Bay than were those detected in birds from the other areas. Perhaps most of these birds spend the entire season in Florida Bay where they probably are exposed to a lower level of contamination. However, we currently have no explanation for the similar magnitude of residues in young of the year from all areas. The pelicans may winter in areas other than those in which they breed (*26*). This is particularly probable of pelicans breeding in South Carolina; most of the birds winter on the east coast of Florida, a few winter in South Carolina, and some winter in Cuba and other southern localities. The east coast and west coast pelicans in Florida generally remain apart from one another. There are no data for birds banded in Florida Bay. Except for birds from Florida Bay, there are no clearcut differences, by locality, in the magnitude of residues in the carcasses; this may be due partly to the small sample size. Residues of DDE and PCB's in carcasses of several of the immature and adult birds seem unduly high, but there is no current basis for associating these residues with adverse biological effects.

EGGSHELL MEASUREMENTS

To determine whether the brown pelican eggshell thickness measurements varied with time in the pre-1947 sample, the Florida thickness measurements were grouped by decade from 1890-1899 to 1930-1939. Thickness by decade ranged from 0.549 mm in the 1920-1929 sample to 0.568 mm in the 1910-1919 sample; an analysis of variance indicated no significant difference ($P>0.05$) between decades (Table 6). Thus all the pre-1947 measurements were combined to compare with the 1969 and 1970 thickness data. There were insufficient measurements in the pre-1947 thickness measurements from South Carolina with which to compare decade differences. Anderson and Hickey (*27*) reported the eggshell thickness of 11 species of birds by decades up to 1939; only one species exhibited significant decade differences.

Comparisons of the 1969 mean shell thickness with the 1970 mean shell thickness of eggs from each of nine

colonies in Florida and two colonies in South Carolina showed that the yearly means were significantly different ($P<0.05$, Student's *t*-test) in only one colony: Boca Grande Pass. The thickness of shells from this colony was 0.559 mm in 1969 compared to 0.517 in 1970.

The eggshell thicknesses of eggs collected in 1970 in Florida and South Carolina were similar to those obtained in 1969 (Tables 7 and 8). The mean eggshell thickness of the Florida eggs collected in 1970 was 0.512 mm, a decrease of 8.1% from the pre-1947 measurements. As in 1969, the thinnest eggs from the southeastern colonies were found in South Carolina; the thickness was approximately 17% less than that of shells in the pre-1947 museum collections. In each State mean eggshell thicknesses for both 1969 and 1970 were significantly less ($P<0.05$) than the pre-1947 eggshell thickness; however, there were no significant differences between the 1969 and 1970 means (Table 8).

The 17% eggshell thinning observed in South Carolina was associated with subnormal reproductive success. We saw several instances of extremely thin eggshells in the South Carolina colonies in both years. Usually, the entire clutch exhibited the extreme thinning, and all the eggs were broken in some nests. The thinnest egg was collected from the Cape Romain colony (33.6% thinner than the pre-1947 mean); it apparently had been laid only hours before collection. Crushing of thinshelled eggs early in the incubation period provides an unknown degree of bias favoring collection of eggs with thicker eggshells.

The mean eggshell thickness of eggs from the Florida Bay colonies varied from 2 to 6% less than the pre-1947 mean. Eggshell thinning in the other two major geographic areas of Florida was somewhat greater: 5 to 8% in the Gulf Coast eggs and about 11% in the Atlantic Coast eggs. It is unknown whether reproduction is impaired when shell thinning reaches 11%.

In this study, we have used eggshell thickness or percentage of pre-1947 thickness in preference to eggshell weight or the thickness index. Each of the four measurements is significantly correlated ($P<0.01$) with the others (Table 9). Therefore it follows that any one of the measurements may be used. An important reason for using thickness is that this is the only measurement that can be taken from crushed or hatched eggs. The reason for using the percentage of the pre-1947 thickness is that thickness measurements for different subspecies or their groups can be combined for analysis of the data; this is not possible using thickness alone due to inherent differences by geographic area in the pre-1947 measurements. It is also possible to compare the relationships between thickness and residue level in eggs of different species. Anderson and Hickey (*27*) found a significant correlation between eggshell weight and thickness index in each of 10 species of birds.

RELATIONSHIP BETWEEN RESIDUES AND EGGSHELL MEASUREMENTS

Most residues in brown pelican eggs have been shown to be significantly correlated with the eggshell measurements (*9*). Mercury was usually positively correlated with the thickness measurements, and in one instance the correlation coefficient was significant ($P<0.05$). By use of stepwise regression, DDE was the only residue that consistently accounted for a significant amount of variability in the three eggshell measurements (*9*). The intimate relationship between DDE and eggshell thinning in the pelican is most impressive, especially considering that the data are taken from wild birds (Fig. 2). Of course, there are natural factors that may influence the thickness of birds' eggshells that were not considered in the analysis. The eggshell thinning potential of certain other pollutants that may occur in pelican eggs has not been thoroughly tested and analytical methods for detecting them are limited. DDE has significantly altered the shell thickness of eggs laid by certain captive birds (*28, 29, 30, 31*), and this compound is universally distributed in wild birds. Thus it is the most likely candidate to be responsible for most of the thinning of eggshells of wild birds. Lead, mercury, and PCB's have been suggested as the shell-thinning agents in the California pelicans; however, residues of mercury and PCB's are no higher in the California eggs than in the southeastern eggs. In all eggs, levels of lead were very low in these eggs and it seems unlikely that lead is responsible for the thinning. Connors et al. (*32*) compared concentrations of nine metals in pelican tissue from Florida and California; residue levels were similar in both areas except that mercury levels were higher in Florida. They considered it unlikely that eggshell thinning and reproductive failure in the brown pelican in California were induced by any of the nine metals.

The rate at which DDE thins eggshells of the brown pelican is greatest when the residues are small (*8*). This relationship is essentially linear on a logarithmic scale.

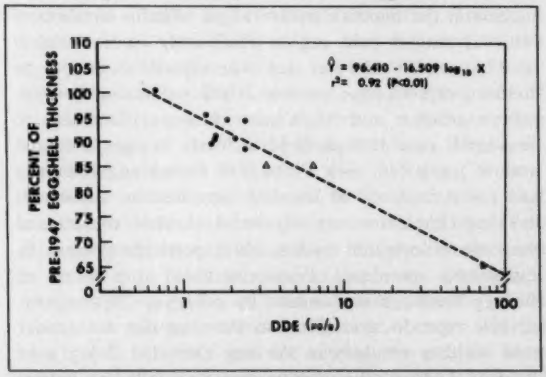

FIGURE 2.—*Association of DDE residues in brown pelican eggs from nine collections in Florida* [•], *two colonies in South Carolina* [Δ], *and one colony in California* [★] *with percent of pre-1947 eggshell thickness.*

The calculated no-effect level is 0.5 μg/g of DDE in the egg, although this level may actually be lower than calculated. Thinning reaches 4% at 1 μg/g, 15% at 5 μg/g, 20% at 10 μg/g, and 40% at 100 μg/g. The logarithmic relationship of DDE to thinning also appeared to be present in the double-crested cormorant (*Phalacrocorax auritus*) (*33*) and the prairie falcon (*Falco mexicanus*) (*34*). Further research is required to define the mathematical relationships of residues to other biological effects.

EFFECTS OF RESIDUES ON REPRODUCTIVE SUCCESS

Data are available from experimental studies that indicate the relationship between eggshell thinning and reproductive success. In experimental studies with DDE in mallards (*Anas platyrhynchos*) and black ducks (*Anas rubripes*) where thinning was less than 18%, increased embryonic mortality, and increased egg breakage were found; both factors resulted in decreased reproductive success (*28, 29*). Other factors associated with eggshell thinning that are found in wild birds are increased egg eating by the parents (*35*), decreased clutch size, and increased embryonic mortality (*36*). It seems likely that DDE is one of the principal agents responsible for the decreased productivity of the pelican in South Carolina (Table 10). However, there are three other pollutants that may have adversely influenced reproductive success. The major suspect is dieldrin. Experimental studies have demonstrated that, even at high residue levels in the egg, dieldrin has little or no effect on eggshell thickness in the mallard (*37*) or ring-necked pheasant (*Phasianus colchicus*) (*38*). However, dieldrin has affected reproductive success in experimental ring-necked pheasants (*39*).

The mean dieldrin level in both South Carolina pelican colonies was near 1 μg/g in 1969. The dieldrin levels in the Cape Romain colony dropped to 0.62 μg/g in 1970. Most of the dieldrin levels in eggs were near the levels thought to cause a lowered reproductive success in the Scottish golden eagle (*Aquila chrysaëtos*) (*40, 41*) and in bald eagles (*Haliaeetus leucocephalus*) in Maine (*42*). Species are not equally sensitive to dieldrin; reproductive success in the gallinules (*Porphyrula martinica* and *Gallinula chloropus*) seemed to be normal even though dieldrin levels in eggs averaged near 4 μg/g (*43, 44*). Potts (*10*) found egg breakage and some evidence of lowered reproductive success in the shag (*Phalacrocorax aristotelis*); dieldrin represented the only chlorinated hydrocarbon pesticide present in appreciable quantities. Potts concluded that much of the egg breakage was caused by polygyny. Apparently, adverse reproductive effects in the shag did not appear until dieldrin residues in the egg exceeded 2 μg/g of dieldrin. These studies demonstrate that different species may respond quite differently to the same toxicant. Judging from the extreme sensitivity of the brown pelican to DDE-induced eggshell thinning, one would suspect that the pelican is also extremely sensitive to dieldrin. However, further study is needed to define this relationship.

PCB's constitute another group of pollutants that may be adversely affecting reproductive success, but this has not been demonstrated in wild birds. The experimental evidence regarding the ability of PCB's to thin eggshells and adversely affect reproductive success is conflicting. In one study with chickens, significant adverse effects on productivity occurred when the chickens were fed 10 and 100 μg/g of Aroclor 1242 or 100 μg/g of Aroclor 1254. The effects were reduced egg production and hatchability and thinning of eggshells (*45*). In a study with mallards, no eggshell thinning or other adverse reproductive effects were observed when Aroclor 1254 was included in the diet at 25 μg/g; bobwhite quail showed no shell thinning or other adverse reproductive effects when fed 50 μg/g of Aroclor 1254 (*46*). Pheasants given a 50-mg capsule dose of Aroclor 1254 weekly for 17 weeks produced fewer eggs than did controls, and significantly more young died while pipping the shell. Chick survival was also adversely affected by Aroclor 1254, but neither eggshell thickness nor fertility was affected (*47*). In ring doves (*Streptopelia risoria*) fed 10 μg/g of Aroclor 1254 for two years, embryonic mortality and chromosomal alterations were found only in the second year (*48*). Although not all the PCB preparations have been tested to determine whether they will thin eggshells, it appears unlikely that they are contributing significantly to thinning in the pelicans (*9*). However, the possibility still exists that the PCB's may also be involved in the lowered reproductive success.

Mercury also may be adversely affecting reproduction in the pelican. In a study with ring-necked pheasants fed 10 μg/g of ethyl mercury p-toluene sulfanonilide, egg production was decreased by 50-80% and embryonic mortality was increased in the few eggs that were laid. Eggshell thickness was not significantly reduced in the birds treated (*49*). In pheasants fed grain treated with methylmercury dicyandiamide, reduced egg production and reduced hatchability occurred. A large number of eggs without shells were found in some groups, but eggshell thickness was not measured (*50*). In another study in which pheasants were fed grain treated with methylmercury dicyandiamide, reduced hatchability was noted after nine days on dosage; eggshell thickness was not measured (*51*). In these studies with pheasants, the mercury level in the eggs ranged from 1.3 to 2.0 μg/g (*51*), from 0.9 to 3.1 (*48*), and from 0.5 to 1.5 μg/g (*50*). In a study with Coturnix quail fed 1 μg/g of mercuric chloride, the eggshell thickness was significantly lower than in controls, yet the eggs contained only 0.06 μg/g of mercury. At the same time, egg production, hatchability, and fertility were unaffected even at a dietary level as high as 8 μg/g (*52*).

In wild birds, Vermeer (*53*) found mercury levels of 0.5 to 2.0 μg/g in eggs collected from successful herring gull clutches; an egg from each of two clutches that produced no young contained 1.3 and 2.4 μg/g. Six of the 21 pelican eggs from South Carolina contained 0.5 μg/g or more of mercury, a level associated with adverse effects on reproductive success in one of the experimental studies with pheasants. Due to differences in species susceptibility, mercury must remain suspect as a causative agent for at least a small portion of the lowered reproductive success in the brown pelican in South Carolina. The herring gull appears to be much more resistant to DDE-induced eggshell thinning (*36*) than the brown pelican. Perhaps the case against mercury weakens when one considers that 16 of the 49 eggs from Florida contained 0.5 μg/g or more mercury, and one on the verge of hatching contained 1.43 μg/g (Table 1). The pelican population in Florida has been considered stable over the past five years, and reproductive success is considered normal (*54*). An occasional egg from the Atlantic Coast of Florida contained levels of dieldrin or DDE that are thought to be deleterious. However, the bulk of the residues in all areas of Florida are low enough that one would not expect these residues to induce widespread, long-term, adverse effects on the populations there.

It is probable that several pollutants are involved in the population decline of brown pelicans in South Carolina. There is a possibility that other pollutants not identified in this study may also have played some role. Storms and high tides have temporarily disrupted nesting activities at times, but the effects of these factors is thought to be minimal because the brown pelican is known to be a persistant renester (*55*). Predation appears to be a minor factor in loss of eggs and young in South Carolina. The islands are isolated, and mammalian predators are not likely to gain access to them. If they did, they would not likely establish permanent residence; cover is sparse, and severe storms sometimes inundate the islands. There are no effective avian egg predators around the colonies except for the herring gull (*Larus argentatus*) and the ring-billed gull (*Larus delawarensis*). These are present in small numbers, and they have not been observed eating pelican eggs. Laughing gulls (*Larus atricilla*) nest in large numbers in each colony, but they apparently have little facility for preying on pelican eggs.

THE POPULATION DECLINE IN SOUTH CAROLINA

Historically, little is known of the numbers of brown pelicans occurring in the colonies in South Carolina; however, we have a fairly good record of the numbers associated with the colony on the Cape Romain National Wildlife Refuge since the 1930's. The pelicans on the Refuge have nested on Marsh Island (Vessel Reef), Bird Bank, White Banks, Cape Island, and Raccoon Key (Sandy Point) at various times in the past; as many as three colony sites on the refuge have been occupied at one time (Table 11).

The breeding population on the Cape Romain National Wildlife Refuge has remained relatively stable through the years. Sprunt and Chamberlain (*55*) reported a maximum of 800 breeding pairs in 1946. However, E. Milby Burton (personal communication) counted over 1,000 nests in one colony on the refuge during the 1930's. The number of estimated nesting pairs on the Cape Romain Refuge ranged from an estimated 500 to 650 from 1962 through 1968; yet a thorough count in 1969 revealed over 1,000 nests.

From 1947 to the early 1960's, Deveaux Bank was apparently the major colony; some interchange of breeding birds apparently occurred between this colony and the Cape Romain colony. There is still apparently a great deal of interchange between the two colonies, but Cape Romain is now the major colony. In 1969, the birds began to nest early on Deveaux Bank, but they deserted in the nest-building phase (T. A. Beckett, III, personal communication), and most of these birds probably moved to Marsh Island. In 1970, nesting pairs increased on Deveaux Bank, and although breeding pairs decreased in the Cape Romain colony, it still contained more breeding birds than Deveaux Bank. With the apparent movement of breeding birds between the two colonies from year to year, population trends in South Carolina seem to be valid only if both colonies are considered together.

Several other islands have been used for nesting sites in South Carolina (Table 11). Existence of some of these colonies is known only from published oological records (*1*) and from data taken from eggs in the Charleston Museum. The record of the pelican colony at the mouth of the Stono River is based on circumstantial evidence, but the island is still in existence and is considered suitable for brown pelican nesting. The exact location of the Bay Point colony near Beaufort, where eggs were collected in 1901, is not known because there are two locations called Bay Point, one on either side of Beaufort. It is not known whether a suitable nesting island is present at either of these locations. Thus pelicans have nested on at least 11 sites in South Carolina. There are relatively few islands in South Carolina that are acceptable to the brown pelican as nesting sites. Two principal requirements of pelican nesting islands seem to be isolation from mammalian predators, particularly raccoons (*Procyon Lotor*), and sufficient elevation of the islands to prevent widescale flooding of nests. Of the two islands currently used for nesting, the pelicans have nested on Marsh Island continuously since 1967 and on Deveaux Bank continuously since about 1946. There are no known nesting records for pelicans on Deveaux Bank until 1946; the Bank was used as a bombing range

in World War II. Marsh Island has been used for nesting at various times since at least 1901. There is some evidence that two colonies of pelicans existed near Beaufort in 1943. A collector (E. J. DeCamps) took eggs from both colonies; he listed one nesting island as Bird Bank, St. Helena Sound (now known as Egg Bank), but he did not list a name for the other island, indicating only that it was 18 miles east of Beaufort. Egg Bank is 12 miles east of Beaufort, while Bay Point (Edisto Island) is approximately 18 miles east of Beaufort. Thus it seems very likely that two colonies existed near Beaufort in 1943, and that pelicans from both colonies moved to Deveaux Bank. Mason (*26*) described the colony on Egg Bank as small, but gave no population estimate.

It seems clear that the pelicans on Deveaux Bank have experienced a drastic population decline beginning at least 10 years ago. With the large nesting population of over 5,000 nesting pairs, the population decline may have progressed for several years before it was noticed. By 1969, the population on Deveaux Bank had dwindled to approximately 250 nesting pairs; the number increased to 479 pairs in 1970. My (L.J.B.) experience with the island since 1969 leads me to believe that space for at least 2,000 to 3,000 nests is currently available.

The most accurate data on the number of breeding birds and reproductive success in South Carolina were obtained in 1969 and 1970. Over this period the number of nests was actually counted except for an estimate for Deveaux Bank in 1969. The number of young fledged was estimated for each colony. According to age-specific mortality data obtained from birds banded during the period 1946 to 1966 in North and South Carolina, approximately 1.2 to 1.5 young must be fledged per breeding female per year in order to maintain a stable population (*56*). Based on this estimate, the number of young fledged in South Carolina in 1969 and 1970 was insufficient to maintain a stable population. The level of eggshell thinning (17%) in South Carolina is within the 15 to 20% level of thinning that has been associated with population declines of certain birds when such thinning occurs consistently over a period of years (*27*). The decline is greater than that recorded in black ducks and mallards fed DDE; these birds have also experienced lowered reproductive success (*28, 29*).

Conclusion

DDE is the agent responsible for all or most of the eggshell thinning of brown pelican eggs observed in all areas where eggs were collected. DDE, because of its propensity for inducing deleterious effects in experimental birds, is suspected of being the principal agent in the lowered reproductive success and resultant population declines in South Carolina and California pelicans. However, other pollutants, particularly dieldrin, may adversely affect reproductive success in ways unrelated to shell thinning.

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TABLE 1.—*Residues of environmental pollutants in brown pelican eggs*

Colony	µG/G (Fresh wet weight)							
	p,p'-DDE	*p,p'*-DDD	*p,p'*-DDT	Dieldrin	PCB's	Mercury	HE [1]	Lead
SOUTH CAROLINA, 1969								
Cape Romain	4.22	0.75	0.77	0.78	5.4	0.65	ND [2]	Tr [3]
	3.64	0.91	0.99	0.60	3.9	0.34	ND	Tr
	5.38	1.79	1.70	1.10	3.8	0.12	ND	Tr
	3.25	1.36	0.83	0.78	4.8	0.29	ND	Tr
	6.55	1.62	1.45	1.63	5.5	0.31	ND	Tr
	4.42	0.94	0.99	1.37	5.7	0.34	ND	Tr
G.M.[4]	4.45	1.17	1.08	0.98	4.79	0.31	—	—
Median	4.32	1.15	0.99	0.94	5.10	0.33	—	—
Deveaux Bank	10.60	2.88	1.86	1.31	11.0	0.26	ND	Tr
	8.70	1.63	ND	0.70	6.6	0.18	ND	Tr
	4.55	1.59	ND	0.60	10.4	0.28	ND	Tr
	6.32	2.21	ND	1.25	5.8	0.26	Tr	Tr
	3.93	1.19	Tr	0.87	3.8	0.25	ND	Tr
G.M.	6.36	1.81	—	0.90	6.99	0.24	—	—
Median	6.32	1.63	—	0.87	6.60	0.26	—	—
SOUTH CAROLINA, 1970								
Cape Romain	0.80	0.20	0.20	0.20	2.0	0.90	ND	NR [5]
	3.30	0.70	0.90	0.80	4.0	0.50	Tr	NR
	2.00	0.80	0.70	0.60	4.0	0.40	ND	NR
	2.30	0.60	0.50	0.50	3.0	0.40	ND	NR
	8.80	0.80	0.70	1.30	6.0	0.30	Tr	NR
	7.80	1.30	0.80	1.30	8.0	0.30	Tr	NR
	3.00	0.80	0.60	1.00	6.0	0.60	Tr	NR
	2.10	0.40	0.50	0.40	4.0	0.50	ND	NR
	1.70	0.50	0.50	0.30	4.0	0.50	ND	NR
	3.70	1.40	0.80	0.90	8.0	0.30	Tr	NR
G.M.	2.83	0.66	0.58	0.62	4.52	0.44	—	—
Median	2.65	0.75	0.65	0.70	4.00	0.45	—	—

TABLE 1.—*Residues of environmental pollutants in brown pelican eggs*—Continued

Colony	μg/g (Fresh wet weight)							
	p,p'-DDE	*p,p'*-DDD	*p,p'*-DDT	Dieldrin	PCB's	Mercury	HE[1]	Lead
FLORIDA ATLANTIC COAST, 1969								
Port Orange	1.72	0.24	0.45	ND	1.7	0.48	ND	Tr
	0.16	0.34	0.12	ND	6.9	0.35	ND	Tr
	5.93	1.74	Tr	0.39	7.1	0.23	ND	Tr
	2.36	1.53	ND	0.66	2.7	0.37	ND	Tr
	1.77	1.07	0.41	0.75	5.3	0.12	ND	Tr
G.M.	1.47	0.75	0.14	0.22	4.12	0.28	—	—
Median	1.77	1.07	0.12	0.39	5.30	0.35	—	—
Cocoa Beach	4.03	1.18	0.88	1.52	7.5	0.20	0.10	Tr
	2.37	0.80	0.56	0.39	2.4	0.44	ND	Tr
	3.49	0.81	0.90	0.67	4.6	0.36	ND	Tr
	3.07	0.92	0.67	0.89	7.4	0.29	Tr	Tr
	0.92	0.18	0.42	0.29	1.3	1.48	ND	Tr
G.M.	2.48	0.66	0.66	0.63	3.80	0.42	—	—
Median	3.07	0.81	0.67	0.67	4.60	0.36	—	—
Pelican Island	1.14	1.99	0.66	0.55	1.3	0.39	0.29	Tr
	2.28	1.75	0.56	0.57	2.8	0.22	ND	Tr
	1.06	0.19	0.30	0.10	1.4	0.41	ND	Tr
	2.48	0.67	0.99	0.32	2.4	0.36	Tr	Tr
	6.01	1.98	0.22	1.09	5.5	0.34	Tr	Tr
G.M.	2.10	1.00	0.47	0.41	2.32	0.34	—	—
Median	2.28	1.75	0.56	0.55	2.40	0.36	—	—
Fort Pierce	2.81	1.09	0.67	0.57	3.9	0.48	ND	Tr
	2.11	0.83	0.30	0.54	1.9	0.68	ND	Tr
	1.54	0.72	0.38	0.20	1.4	0.70	ND	Tr
	3.39	0.97	0.67	0.28	2.4	0.52	ND	Tr
	3.15	1.01	0.66	0.25	2.5	0.57	ND	Tr
	3.00	1.23	0.67	0.31	1.9	0.16	ND	Tr
	1.74	0.83	0.56	0.26	1.0	0.38	ND	Tr
G.M.	2.44	0.94	0.54	0.32	1.98	0.46	—	—
Median	2.81	0.97	0.66	0.26	1.90	0.52	—	—
FLORIDA GULF COAST, 1969								
Cedar Key	0.98	0.31	0.20	Tr	Tr	0.47	ND	Tr
	0.85	0.31	0.14	Tr	Tr	0.16	ND	Tr
	0.84	0.41	0.22	0.15	Tr	0.18	ND	Tr
	5.54	0.96	0.39	Tr	4.2	0.35	ND	Tr
	1.65	0.59	0.30	0.12	1.4	0.31	ND	Tr
	1.00	0.20	0.27	Tr	Tr	0.48	ND	Tr
	1.32	0.23	0.26	Tr	1.2	0.49	ND	Tr
G.M.	1.36	0.37	0.24	0.08	0.89	0.32	—	—
Median	1.00	0.31	0.26	0.05	0.50	0.35	—	—
Pinellas	1.23	0.63	0.44	0.13	1.6	0.40	Tr	Tr
	1.72	0.65	0.52	0.26	1.8	0.17	Tr	Tr
	2.44	0.99	0.57	0.27	1.5	0.41	Tr	Tr
	3.78	1.95	ND	0.40	2.9	1.21	Tr	Tr
	1.42	0.62	0.54	Tr	1.1	0.66	ND	Tr
G.M.	1.94	0.87	0.32	0.18	1.69	0.47	—	—
Median	1.72	0.65	0.52	0.26	1.60	0.41	—	—
Boca Grande Pass	1.18	0.29	ND	0.11	Tr	0.43	ND	Tr
	0.46	0.12	0.11	Tr	Tr	0.16	ND	Tr
	0.78	0.23	ND	Tr	Tr	0.42	ND	Tr
	0.70	0.36	0.24	0.21	Tr	0.45	ND	Tr
	0.52	0.15	0.22	Tr	Tr	0.40	ND	Tr
G.M.	0.69	0.22	0.11	0.09	0.50	0.35	—	—
Median	0.70	0.23	0.11	0.05	0.50	0.42	—	—
Hemp Island	1.76	0.37	0.33	0.17	2.0	0.24	ND	Tr
	1.87	0.45	0.52	Tr	Tr	0.59	ND	Tr
	1.86	0.65	0.52	0.15	Tr	0.78	ND	Tr
	1.19	0.24	0.19	Tr	Tr	0.62	ND	Tr
	1.66	0.52	0.32	0.11	Tr	0.86	ND	Tr
G.M.	1.65	0.42	0.35	0.09	0.66	0.57	—	—
Median	1.76	0.45	0.33	0.11	0.50	0.62	—	—
Matlacha	1.32	0.19	0.22	Tr	1.0	0.75	ND	Tr
	3.01	1.51	0.71	Tr	2.3	1.47	Tr	Tr
	1.44	1.02	0.39	0.22	1.4	0.86	ND	Tr
	2.17	0.70	0.39	0.10	1.0	0.82	ND	Tr
	0.90	0.28	0.21	Tr	Tr	0.50	ND	Tr
G.M.	1.62	0.56	0.35	0.08	1.10	0.83	—	—
Median	1.44	0.70	0.39	0.05	1.00	0.82	—	—

TABLE 1.—*Residues of environmental pollutants in brown pelican eggs*—Continued

Colony	μg/g (Fresh wet weight)							
	p,p'-DDE	*p,p'*-DDD	*p,p'*-DDT	Dieldrin	PCB's	Mercury	HE [1]	Lead
FLORIDA, FLORIDA BAY, 1970								
Nest Key	0.81	ND	ND	ND	1.1	0.98	ND	Tr
	0.65	0.16	ND	ND	Tr	0.29	ND	Tr
	1.59	0.34	0.17	0.28	2.5	0.78	ND	Tr
	0.90	0.12	ND	ND	0.6	0.38	ND	Tr
	1.72	0.36	0.16	Tr	1.4	0.84	ND	Tr
G.M.	1.05	0.16	—	—	0.9	0.59	—	—
Median	0.90	0.16	—	—	1.1	0.78	—	—
Buchanan Key	2.87	0.50	0.35	0.33	2.7	0.94	ND	Tr
	0.62	0.13	ND	ND	Tr	0.59	ND	Tr
	1.66	0.10	ND	0.15	1.8	0.86	ND	Tr
	0.51	0.18	ND	ND	Tr	0.49	ND	Tr
	1.15	0.20	0.13	0.14	1.3	0.94	ND	Tr
G.M.	1.11	0.19	—	—	0.8	0.74	—	—
Median	1.15	0.18	—	—	1.3	0.86	—	—
Fanny Key	0.56	0.15	ND	ND	Tr	0.51	ND	Tr
	0.68	0.10	ND	ND	Tr	0.47	ND	Tr
	0.96	0.21	ND	ND	0.6	0.09	ND	Tr
	0.40	Tr	ND	ND	Tr	0.57	ND	Tr
	1.64	0.23	0.24	ND	2.1	0.11	ND	Tr
G.M.	0.75	0.13	—	—	0.5	0.27	—	—
Median	0.68	0.15	—	—	Tr	0.47	—	—
Marquesas Key	1.07	0.12	0.15	ND	Tr	0.35	ND	Tr
	0.82	ND	0.11	ND	Tr	0.45	ND	Tr
	1.46	0.14	0.25	ND	Tr	0.53	ND	Tr
	1.20	0.14	0.12	ND	Tr	0.45	ND	Tr
	1.45	0.14	0.16	ND	1.1	0.54	ND	Tr
G.M.	1.17	0.11	0.15	—	0.3	0.46	—	—
Median	1.20	0.14	0.15	—	Tr	0.45	—	—
CALIFORNIA, 1969								
Anacapa [6]	76.1	1.3	1.9	0.2	8.0	0.42	ND	Tr
	50.6	1.4	1.9	0.1	5.0	0.36	ND	Tr
	135.0	2.4	3.8	0.2	12.0	0.31	ND	Tr
	60.2	0.3	0.6	Tr	3.2	0.17	ND	Tr
	39.5	0.5	1.2	Tr	Tr	0.40	ND	Tr
	97.8	3.4	4.6	0.1	8.0	0.30	ND	Tr
	63.2	1.3	1.6	Tr	5.0	0.56	ND	Tr
	65.0	0.9	1.5	Tr	Tr	0.34	ND	0.17
	70.0	1.3	1.4	Tr	6.0	0.31	ND	Tr
	98.4	1.5	1.9	0.2	4.0	0.33	ND	Tr
G.M.	71.35	1.18	1.76	0.09	3.60	0.34	—	0.06
Median	67.50	1.30	1.90	0.08	5.00	0.34	—	0.05

[1] HE = Heptachlor epoxide.
[2] ND = No residue detected.
[3] Tr = Trace of residue; a trace is considered <1.0 μg/g for PCB's and <0.1 μg/g for all other residues.
[4] G.M. = Geometric Mean.
[5] NR = Analysis not run.
[6] Each of the 10 eggs from California contained from trace to 0.2 μg/g of both *o,p'*-DDT and *o,p'*-DDD.

TABLE 2.—*Comparisons of brown pelican egg residues by geographic areas, 1969*

Area	Number of Eggs	Geometric mean (μg/g)[1]					
		p,p'-DDE	*p,p'*-DDD	*p,p'*-DDT	Dieldrin	PCB's	Mercury
Florida Gulf Coast	27	1.37 A [2] (1.09-1.72)	0.43 A (0.33-0.57)	0.25 A (0.19-0.34)	0.10 A (0.07-0.12)	0.89 A (0.68-1.16)	0.46 A (0.36-0.57)
Florida Atlantic Coast	22	2.24 B (1.60-3.13)	0.83 B (0.61-1.14)	0.40 A (0.27-0.60)	0.36 B (0.24-0.53)	2.81 B (2.11-3.74)	0.37 AB (0.29-0.48)
South Carolina	11	5.24 C (4.08-6.72)	1.43 C (1.09-1.87)	0.37 A (0.13-1.09)	0.94 C (0.77-1.16)	5.68 C (4.45-7.26)	0.28 B (0.21-0.36)
California	10	71.70 D (55.38-91.93)	1.18 BC (0.71-1.94)	1.76 B (1.17-2.65)	0.09 A (0.06-0.14)	3.60 BC (1.63-7.95)	0.42 AB (0.24-0.71)

[1] 95% confidence limits in parentheses.
[2] A significant difference ($P<0.05$) among means of a chemical is indicated for those residues not sharing a common letter. Means were separated using Duncan's New Multiple Range test with Kramer's extension for unequal replication. (*Kramer, C. Y. 1956.* Extension of multiple range tests to group means with unequal numbers of replications. Biometrics, 12: 307-310.)

TABLE 3.—*Association of egg residues with one another, egg basis*

Chemical	Simple correlation coefficient				
	DDD	DDT	Dieldrin	PCB's	Mercury
CALIFORNIA					
DDE	0.698 [1]	0.679 [1]	0.688 [1]	0.655 [1]	−0.153
DDD	—	0.950 [2]	0.577	0.620	0.350
DDT	—	—	0.609	0.500	0.310
Dieldrin	—	—	—	0.583	0.076
PCB's	—	—	—	—	−0.050
SOUTH CAROLINA					
DDE	0.835 [2]	0.038	0.845 [2]	0.751 [2]	−0.698 [2]
DDD	—	−0.037	0.767 [2]	0.732 [2]	−0.803 [2]
DDT	—	—	0.259	−0.010	0.100
Dieldrin	—	—	—	0.618 [2]	−0.555 [2]
PCB's	—	—	—	—	−0.401
FLORIDA					
DDE	0.732 [2]	0.314 [1]	0.531 [2]	0.559 [2]	0.032
DDD	—	0.272	0.647 [2]	0.632 [2]	−0.025
DDT	—	—	0.262	0.239	0.033
Dieldrin	—	—	—	0.610 [2]	−0.245
PCB's	—	—	—	—	−0.217

[1] $P<0.05$
[2] $P<0.01$

TABLE 4.—*Residues of environmental pollutants in an adult male bown pelican that died in tremors*

Chemical	µG/G (wet weight)	
	Carcass	Brain
p,p'-DDE	11.04	11.30
p,p'-DDD	2.80	2.17
p,p'-DDT	0.31	1.26
Dieldrin	1.24	1.82
HE	Tr	Tr
PCB's	20.0	10.0
Mirex	NR	NR
Mercury	1.57	NR

TABLE 5.—*Residues of environmental pollutants in carcasses of brown pelicans*

Approximate Age	Sex	µG/G (wet weight)					
		p,p'-DDE	*p,p'*-DDD	*p,p'*-DDT	Dieldrin	PCB's	Mirex
SOUTH CAROLINA							
1 week	unk [1]	0.79	ND	ND	0.19	1.3	ND
6 weeks	♀	0.20	ND	ND	ND	Tr	ND
6 weeks	unk	0.29	ND	ND	ND	Tr	ND
Immature	♀	9.20	0.74	0.12	1.50	19.0	0.22
Adult	♂	25.20	0.84	0.38	0.84	35.0	1.06
FLORIDA: ATLANTIC COAST							
4 weeks	♀	0.10	ND	ND	ND	Tr	ND
10 weeks	unk	0.37	1.21	0.51	0.44	7.5	ND
13 weeks	♂	1.35	0.54	ND	0.34	3.3	ND
Immature	♀	15.00	1.90	0.69	1.60	29.0	0.20
Adult	♀	8.00	0.76	ND	0.61	12.0	0.20
FLORIDA: FLORIDA BAY							
3 weeks	unk	0.34	ND	ND	ND	Tr	ND
7 weeks	♀	0.29	ND	ND	ND	Tr	ND
Immature	♂	1.20	0.46	0.12	0.13	1.0	ND
Adult	♂	3.65	0.70	0.38	0.47	4.4	ND
Adult	♀	1.20	0.38	ND	ND	3.0	ND
FLORIDA: GULF COAST							
1 week	unk	0.13	ND	ND	ND	Tr	ND
4 weeks	unk	0.26	0.10	0.79	ND	1.2	ND
14 weeks	♀	1.00	1.10	0.17	0.29	3.5	0.17
Immature [2]	♂	4.55	0.84	ND	0.60	19.0	0.31
Immature	♂	31.00	1.90	1.20	1.80	34.0	0.30
Adult	♀	9.60	0.63	ND	0.74	19.5	1.45

[1] Sex not determined.
[2] Sick bird.

TABLE 6.—*Brown pelican pre-1947 eggshell thickness by decades, Florida*

Decade	Number of Eggs	Thickness, mm
		Mean + Standard Error
1890-1899	44	0.560 ± 0.006 [1]
1900-1909	12	0.566 ± 0.008
1910-1919	33	0.568 ± 0.007
1920-1929	39	0.549 ± 0.005
1930-1939	38	0.553 ± 0.006

[1] Means not significantly different (P>0.05) as tested using analysis of variance. Eggs from 1880-1889 omitted due to small sample size.

TABLE 7.—*Thicknesses of brown pelican eggshells from 17 colonies, 1970*

Colony	Number of Eggs	Mean Thickness[1], mm
SOUTH CAROLINA		
Deveaux Bank	20	0.460 ± 0.011 A [2]
Cape Romain (Marsh Island)	18	0.461 ± 0.009 A
FLORIDA		
Cocoa Beach (Hall Island)	10	0.482 ± 0.019 AB
Pinellas (Tarpon Key)	10	0.487 ± 0.015 ABC
Crane Island	10	0.491 ± 0.009 ABC
Port Orange	9	0.497 ± 0.009 ABCD
Pelican Island	9	0.498 ± 0.017 ABCD
Cortez	10	0.502 ± 0.012 BCD
Matlacha Pass	10	0.504 ± 0.019 BCD
Fort Pierce	9	0.504 ± 0.009 BCD
Boca Grande Pass (Bird Key)	10	0.517 ± 0.014 BCD
Hemp Island	10	0.519 ± 0.015 BCD
Fanny Key	7	0.523 ± 0.019 BCD
Cedar Key (Seahorse Key)	10	0.531 ± 0.016 CD
Nest Key	10	0.532 ± 0.012 CD
Marquesas Key	10	0.541 ± 0.012 D
Buchanan Key	10	0.545 ± 0.013 D

[1] Mean ± standard error.
[2] A significant difference (P<0.05) among thickness means is indicated for those means not sharing a common letter. Means were separated using Duncan's New Multiple Range Test with Kramer's extension for unequal replication. (See footnote 2, Table 2.)

TABLE 8.—*Thicknesses of brown pelican eggshells, comparisons of pre-1947, 1969, and 1970 measurements*

Mean thickness + standard error		
Pre-1947 [1]	1969	1970
SOUTH CAROLINA		
0.557 ± 0.010 (23) A [2]	0.463 ± 0.006 (49) B	0.461 ± 0.007 (38) B
FLORIDA		
0.557 ± 0.003 (172) A	0.515 ± 0.005 (81) B	0.512 ± 0.004 (144) B

[1] Sample size in parentheses.
[2] A significant difference (P<0.05) among thickness means for each state is indicated for those means not sharing a common letter. Means were separated using Duncan's New Multiple Range Test with Kramer's extension for unequal replication. (See footnote 2, Table 2.)

TABLE 9.—*Association of eggshell measurement parameters with one another, egg basis*

Parameter	Simple correlation coefficient [1]		
	Weight	Thickness Index	Percent of Pre-1947 Thickness
FLORIDA, SOUTH CAROLINA, AND CALIFORNIA			
Thickness	0.832	0.893	0.998
Weight	—	0.849	0.831
Thickness Index	—	—	0.903

[1] P<0.01

TABLE 10.—*Reproductive success of brown pelicans in South Carolina, 1969-70*

Year	Colony	Number of Nests	Number of Young Fledged	Young Fledged per Nest
1969	Cape Romain	1016	900	0.82
	Deveaux Bank	250	80	0.32
Totals or mean		1266	980	0.78
1970	Cape Romain	637	500	0.78
	Deveaux Bank	479	445	0.93
Totals or mean		1116	945	0.85

TABLE 11.—*Islands used for nesting by the brown pelican in South Carolina*

Island	Year
Unidentified, Georgetown County	1934 [1]
Raccoon Key (Sandy Point)	1931 [2]; 1943-1946; 1952 [3]
Cape Island	1939-1942 [3]
White Banks	1956; 1958-1960; 1963; 1965 [3]
Marsh Island (Vessel Reef)	1947-1948; 1951; 1955-1959; 1962; 1964-1965; 1967 through 1972 [3]
Bird Bank	1901; 1915 [1]; 1926 [4]; 1928 [2]; 1951; 1957-1961; 1963; 1965-1966 [3]
Unidentified, on beach near Charleston	1901 [1]
Bird Key (mouth of Stono River)	Unknown [5]
Deveaux Bank	1947 through 1972 [6]
Egg Bank (near Beaufort, also called Bird Bank)	1904 [4]; 1943 [1]
Unidentified, 18 mi. east of Beaufort	1943 [1]
Bay Point (large colony)	1901 [1]

[1] Anderson and Hickey (see LITERATURE CITED, reference 1).
[2] E. Milby Burton (personal communication).
[3] Records of the Cape Romain National Wildlife Refuge. I (L.J.B.) have visited the Marsh Island colony each year since 1969.
[4] Data taken from egg collection in Charleston Museum.
[5] Robert Gracy (personal communication: people associated with this area informed him that pelicans once nested here).
[6] Beckett (see LITERATURE CITED, reference 2). I (L.J.B.) visited this colony each year since 1969.

Residues of Organochlorine Pesticides, Mercury, and PCB's in Mourning Doves from Eastern United States—1970-71

J. F. Kreitzer[1]

ABSTRACT

Mourning dove (Zenaidura macroura) *breast muscle samples from birds collected in 1970-71 from Rhode Island, Pennsylvania, Maryland, Missouri, Kentucky, Virginia, Arkansas, Tennessee, North Carolina, South Carolina, Mississippi, Alabama, Georgia, Louisiana, and Florida were found to contain residues of DDT, DDE, DDD, polychlorinated biphenyls, dieldrin, mirex, mercury, and heptachlor epoxide in amounts not considered hazardous to consumers, human or nonhuman. There were 145 birds involved, 7 to 10 from each State. Residues of DDT plus DDE plus DDD averaged 5.83 ppm lipid weight (0.068 ppm wet weight); those of PCB's, 9.75 ppm lipid weight (0.121 ppm wet weight); compounds were found in all birds. Heptachlor epoxide and dieldrin were found in little more than trace amounts: heptachlor in all birds, dieldrin in 73. Mirex was found only in birds from South Carolina, Georgia, and Florida, averaging 4.32 ppm lipid weight (0.046 ppm wet weight) in eight birds. Less than 0.05 ppm (wet weight) mercury was found in all birds except 10, in which it ranged from 0.07 to 0.67 ppm. The 10 were from Rhode Island, Pennsylvania, Maryland, Virginia, Tennessee, and Alabama.*

Introduction

This paper reports the residues of organochlorine pesticides, polychlorinated biphenyls, and mercury in mourning doves (*Zenaidura macroura*) of the eastern United States. The study was undertaken to determine whether the small but steady decline of mourning dove populations in the United States during 1960-1970 (Migratory Bird Populations Station, unpublished data) might be related to environmental contaminants, and whether the level of these contaminants in the tissues need cause concern for their consumption as human food.

Certain game birds have been found to contain undesirably high levels of toxicants. For example, 28 of 32 pheasants (*Phasianus colchicus*) found dead or dying in Sweden, 1957-1963, contained between 25 and 140 ppm mercury in liver and kidney tissues, and 16 of 27 pheasants shot or trapped during the same period contained more than 1 ppm (range: 1-20 ppm) (*1*).

In 1970, the Canadian government closed the hunting season for woodcock (*Philohela minor*) in New Brunswick because of an average level of 56 ppm DDT (lipid basis) in representative samples taken throughout the Province. In 1969, the Province of Alberta closed the seasons for pheasant (*Phasianus colchicus*) and Hungarian partridge (*Perdix perdix*) because of high levels of mercury in the liver; residues averaged 2.8 ppm in pheasants and 1.1 ppm in partridges (*2*). Although the season was not closed for sharp-tailed grouse (*Pedioecetes phasianellus*), concentrations of mercury in the liver were as high as 1.1 ppm.

In western Montana 73 samples of fatty tissues from 69 blue grouse (*Dendragapus obscurus*), collected ½ to 685 days after their range had been sprayed with DDT at ½ lb/acre, contained DDT-derived residues ranging from 0.9 to 280 ppm (*3*). In this instance the U.S. DHEW Food and Drug Administration recommended that persons eating game from pesticide-treated areas be warned to trim away fat to the extent practical and thereby reduce exposure to such residues.

Materials and Methods

Birds were collected from all States east of the Mississippi that permit the hunting of mourning doves, except for Illinois, Delaware, and West Virginia. Eastern samples came from Rhode Island, Pennsylvania, Mary-

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land, Kentucky, Tennessee, Virginia, North Carolina, South Carolina, Mississippi, Alabama, Georgia, and Florida. Three dove-hunting states west of the Mississippi were also included: Missouri, Arkansas, and Louisiana. Ten birds were taken from each State except for Arkansas and Virginia which produced nine each, and Pennsylvania, which produced seven. Thus 145 birds were available for tissue analysis.

Carcasses were frozen at the time of collection. At preparation of the samples they were partly thawed and a 10-g sample of breast muscle was taken from each. Samples were placed in a glass jar that had been cleaned with nitric acid, acetone, and hexane; then they were refrozen.

Analyses were made at WARF Institute, Inc., Madison, Wisconsin, by the following methods:

For organochlorines and PCB's, samples were weighed, dried at 40°C for 72-96 hours, reweighed, then ground with sodium sulfate and extracted with petroleum ether:ethyl ether (170 ml:70 ml) on a Soxhlet extractor for 8 hours. They were cleaned and separated into two fractions by passage through a Florisil Column (petroleum ether:ethyl ether, 95:5, 85:15). An aliquot of the sample was passed through a standardized silicic acid-celite column, with typical elutions of 260 ml petroleum ether:210 ml 1:19:80 acetonitrile:hexane:dichloromethane. Analysis was by a Barber-Coleman Pesticide Analyzer Model 5360. The column was glass, 4 ft by 4 mm, packed with 5% DC-200°C (column), and 240°C (detector); carrier gas was nitrogen at a flow rate that eluted *p,p'*-DDT in 6-8 minutes. Lipid weight was determined from an aliquot of the extract which was reduced to dryness on a stream bath and placed in a 40°C oven for 2 to 4 hours before weighing. Three-column confirmations of compounds found were made on a random selection of tissue samples.

Total mercury was determined by cold vapor atomic absorption. A 10-g portion was digested by refluxing with sulfuric nitric acid mixture (*4*). A mixture of hydroxylamine, stannous chloride, and sulfuric acid was added to the digest to reduce the mercury (II) ions to mercury metal. The sample was aerated (3 liters/min) and passed through the absorption cell.

Recoveries of organochlorine pesticides from spiked samples were 75-105%; those of PCB's (based on Aroclor 1254) were 60-85%; and those of mercury were 95%. Residues were not corrected for recovery. The limit of sensitivity was from 0.001 to 0.006 ppm for organochlorines, and 0.05 ppm for mercury.

Analyses of variance were made using log transformations.

Results and Discussion

Results of analyses are in Tables 1 and 1A. Means given in the tables and in the text are arithmetic. Locations of collection sites with corresponding concentrations of DDE and PCB in the birds are shown in Figures 1 and 2.

Because of the low residues in many samples and the numerous "less than" values, overall means were computed only for DDT and its metabolites (DDE and DDD), mirex, and PCB's. Means were: 5.83 ppm lipid weight (0.068 ppm wet weight) DDT (including metabolites); 4.32 ppm lipid weight (0.046 ppm wet weight) mirex; and 9.75 ppm lipid weight (0.121 ppm wet weight) PCB's. Statistical comparisons were possible only for DDE and PCB's (Table 2). These comparisons are strictly between collecting sites, not between states: the sites were not selected at random. There were no clearcut differences between northern sites and southern sites or between other geographical regions.

Mercury was found in small amounts, less than 0.05 ppm (wet weight) except in 10 birds in which it ranged from 0.07 to 0.67 ppm. The 10 were from Pennsylvania, Rhode Island, Maryland, Alabama, Tennessee and Virginia. Heptachlor epoxide and dieldrin were found in little more than trace amounts in most birds; only a few birds contained more than 1 ppm. Amounts of heptachlor epoxide ranged from 0.14 to 8.70 ppm lipid weight (<0.006 to 0.170 ppm wet weight), and those of dieldrin, from 0.11 to 10.22 ppm lipid weight (0.001 to 0.160 ppm wet weight).

DDT and its metabolites, PCB's, heptachlor epoxide, and mercury were found in all birds; dieldrin was found in 73; and mirex in 8.

The relatively small amounts of these compounds in the birds suggest there is little hazard, if any, to the birds themselves, or to the consumers, human or nonhuman, of the birds flesh. The amount of DDT and its metabolites does approach the amount of DDT permitted in ground beef by Federal regulations (7 ppm in the fat). But since dove meat has so little fat (1.3% in the tissues analyzed), an individual would have to eat nearly 26 pounds of it to ingest the amount of the pesticide permitted in 1 pound of hamburger. About 550 doves would be required.

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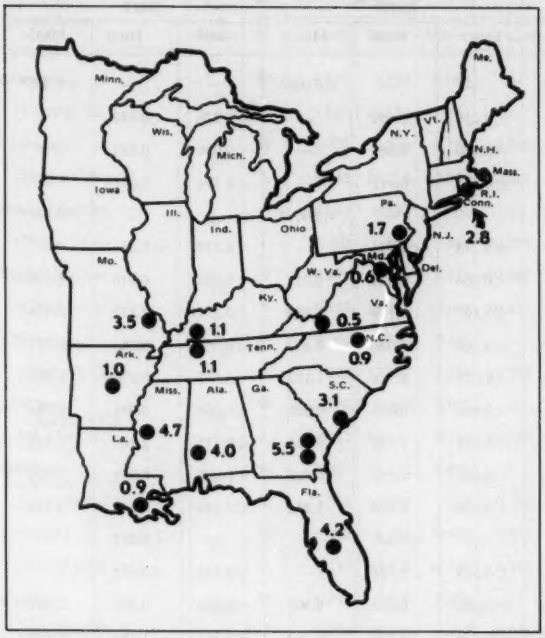

FIGURE 1.—*Mean (geometric) concentration of DDE (lipid basis) in breast muscle of mourning doves, 1970-71*[1]

[1] Dots show approximate sites of collection.

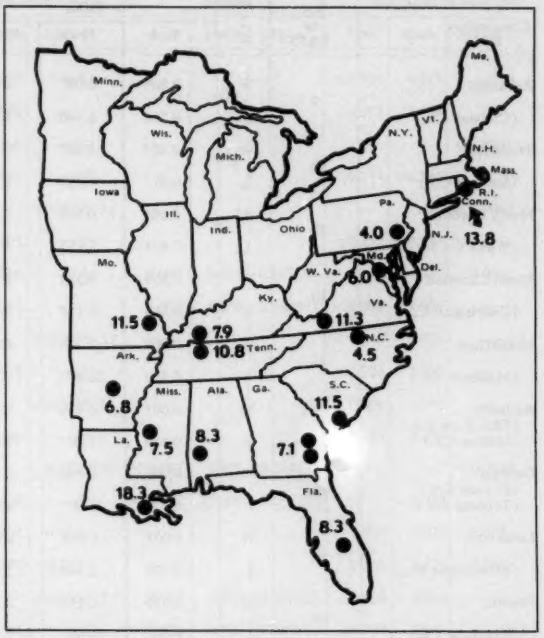

FIGURE 2.—*Mean (geometric) concentration of PCB (lipid basis) in breast muscle of mourning doves, 1970-71*[1]

[1] Dots show approximate sites of collection.

TABLE 1.—*Residues of DDE, DDD, and DDT in breast muscle of mourning doves from 15 eastern hunting states, 1970-71*

Collection Site	No. of Birds	Wt. Basis	Residues, ppm								
			DDE			DDD			DDT		
			Low	High	Mean	Low	High	Mean	Low	High	Mean
Rhode Island	10	W	0.010	0.160	0.050	<0.006	0.034	0.008	<0.006	0.008	0.006
(Washington Co.)		L	0.550	9.898	3.072	<0.168	2.774	0.522	<0.144	0.561	0.351
Pennsylvania	7	W	0.006	0.440	0.084	<0.006	0.009	0.006	<0.006	0.011	0.006
(Berks Co.)		L	0.411	38.52	6.002	<0.223	0.632	0.412	<0.223	0.632	0.439
Maryland	10	W	<0.005	0.047	0.014	—	—	<0.006*	—	—	<0.006*
(Anne Arundel Co.) (Prince Georges Co.)		L	<0.175	4.338	0.962	<0.175	<0.938	—	<0.175	0.938	—
Missouri	10	W	0.021	0.220	0.073	<0.006	0.034	0.013	<0.006	0.064	0.013
(Cape Girardeau Co.)		L	2.555	10.44	4.984	<0.361	2.446	0.865	<0.400	3.218	1.371
Kentucky	10	W	<0.006	0.024	0.013	—	—	<0.006*	—	—	<0.006*
(Trigg Co.)		L	0.366	1.275	0.864	<0.235	<0.463	—	<0.235	<0.463	—
Virginia	9	W	<0.006	0.071	0.015	—	—	<0.006*	—	—	<0.006*
(Montgomery Co.)		L	0.273	7.350	1.466	0.273	<0.674	—	<0.273	<0.899	—

TABLE 1.—*Residues of DDE, DDD, and DDT in breast muscle of mourning doves from 15 eastern hunting states, 1970-71 —Continued*

Collection Site	No. of Birds	Wt. Basis	Residues, ppm								
			DDE			DDD			DDT		
			Low	High	Mean	Low	High	Mean	Low	High	Mean
Arkansas	9	W	0.006	0.065	0.019	—	—	<0.006*	—	—	<0.006*
(Conway Co.)		L	0.541	6.140	1.730	<0.226	<0.682	—	<0.226	<0.682	—
Tennessee	10	W	0.005	0.085	0.023	<0.006	0.008	—	<0.006	0.012	—
(Stewart Co.)		L	0.417	8.468	1.777	<0.254	0.811	—	<0.254	1.261	—
North Carolina	10	W	0.006	0.039	0.014	—	—	<0.006*	—	—	<0.006*
(Wake Co.)		L	0.471	2.953	1.088	<0.258	<0.531	—	<0.258	<0.531	—
South Carolina	10	W	0.009	0.580	0.026	<0.006	0.024	0.010	<0.006	0.018	0.008
(Charleston Co.)		L	0.806	76.118	7.739	<0.302	3.176	1.020	<0.352	2.471	0.754
Mississippi	10	W	0.009	0.270	0.087	<0.006	0.046	0.012	<0.006	0.063	0.013
(Madison Co.)		L	0.559	26.415	7.724	<0.373	4.528	1.132	<0.132	6.226	1.219
Alabama (Chocktaw Co.) (Mobile Co.)	10	W	0.007	0.810	0.126	<0.006	0.013	0.008	<0.006	0.044	0.014
		L	0.389	78.00	11.490	<0.333	1.181	0.628	<0.333	2.835	1.182
Georgia (Oconee Co.) (Toombs Co.)	10	W	0.008	0.400	0.122	<0.006	0.050	0.016	<0.006	0.008	0.006
		L	0.678	35.60	9.379	<0.339	3.670	1.231	<0.339	3.511	1.234
Louisiana	10	W	<0.003	0.013	0.008	—	<0.007	—	—	<0.007	—
(Terrebonne Co.)		L	<0.220	2.368	1.064	<0.330	<0.882	—	<0.330	<0.882	—
Florida	10	W	0.010	0.250	0.089	<0.006	0.032	0.008	<0.006	0.150	0.008
(Highland Co.)		L	0.991	25.69	7.756	<0.444	3.303	0.732	<0.380	1.193	0.663

W = wet weight; L = lipid weight.
* = All birds reported at this value.
ND = Not detected; value = 0 in computing means.
Numerals in parentheses indicate number of birds in which the compound was not detected.
< quantities taken at face value in computing means.
Means are arithmetic.

TABLE 1A.—*Residues of PCB's, dieldrin, mirex, and heptachlor epoxide in breast muscle of mourning doves from 15 eastern hunting states, 1970-71*

Collection Site	No. of Birds	Wt. Basis	Residues, ppm											
			PCB			Dieldrin			Mirex			Heptachlor epoxide		
			Low	High	Mean	Low	High	Mean	Low	High	Mean	Low	High	Mean
Rhode Island	10	W	0.091	0.520	<0.229	<0.005	0.160	—		ND		<0.006	0.170	—(5)
(Washington Co.)		L	8.867	43.307	14.131	<0.566	10.22	—				<0.143	7.936	—(5)
Pennsylvania	7	W	0.072	0.140	0.102	<0.005	0.016	—		ND		<0.006	0.021	—(2)
(Berks Co.)		L	3.234	9.895	7.027	<0.526	1.012	—				<0.223	1.310	—(2)
Maryland (Anne Arundel Co.) (Prince Georges Co.	10	W	0.046	0.180	0.088	—	—	0.005*(8)		ND		—	—	<0.006*
		L	3.179	21.406	5.929	<0.298	<0.781	—				<0.175	0.411	—
Missouri	10	W	0.093	0.280	0.153	0.005	0.077	0.016		ND		<0.006	0.027	—(1)
(Cape Girardeau Co.)		L	4.760	31.609	13.320	0.361	2.299	1.083				<0.361	3.103	—(1)
Kentucky	10	W	0.061	0.200	0.118		ND			ND		—	—	<0.006*
(Triggs Co.)		L	4.573	15.583	8.326							<0.235	<0.500	—
Virginia	9	W	0.110	0.240	0.164		ND			ND		—	—	<0.006*
(Montgomery Co.)		L	8.864	23.810	15.520							<0.272	<0.674	—

TABLE 1A.—*Residues of PCB's, dieldrin, mirex, and heptachlor epoxide in breast muscle of mourning doves from 15 eastern hunting states, 1970-71*—Continued

Collection Site	No. of Birds	Wt. Basis	Residues, ppm											
			PCB			Dieldrin			Mirex			Heptachlor epoxide		
			Low	High	Mean	Low	High	Mean	Low	High	Mean	Low	High	Mean
Arkansas	9	W	0.073	0.170	0.089	—	0.006	—(8)		ND		<0.006	0.015	—
(Conway Co.)		L	3.860	16.367	7.201	—	0.526	—(8)				<0.382	1.404	—
Tennessee	10	W	0.075	0.240	0.164	<0.005	0.006	—(5)		ND		—	—	<0.006*
(Stewart Co.)		L	6.042	24.234	12.320	<0.212	0.631	—(5)				<0.254	<0.541	—
North Carolina	10	W	0.042	0.082	0.061	—	—	<0.005*(8)		ND		—	—	<0.006*
(Wake Co.)		L	3.100	6.351	4.654	<0.258	<0.462	—(8)				<0.257	<0.531	—
South Carolina	10	W	0.086	0.160	0.121	<0.005	0.024	—(2)	0.005	0.039	0.007(8)	—	—	<0.006*
(Charleston Co.)		L	5.324	18.229	12.004	<0.251	3.012	—(2)	0.602	4.234	2.680(8)	<0.302	<1.008	—
Mississippi	10	W	<0.060	0.660	0.145	—	—	<0.005*(5)		ND		<0.006	0.015	—
(Madison Co.)		L	3.263	17.981	8.044	<0.313	<0.658	—(5)				<0.373	1.578	—
Alabama	10	W	0.033	0.088	0.071	—	—	<0.005*(6)		ND		<0.006	0.091	—
(Chocktaw Co.) (Mobile Co.)		L	2.782	13.048	6.168	<0.270	<0.400	—(6)				<0.324	8.696	—
Georgia	10	W	0.047	0.170	0.097	—	—	6.005*(8)	<0.005	0.370	0.124(7)	—	—	<0.006*
(Oconee Co.) (Toombs Co.)		L	3.538	12.067	7.426	<0.249	<0.256	—(8)	<0.282	25.800	9.597(7)	—	0.455	—
Louisiana	10	W	0.060	0.220	0.121	0.001	0.002	0.002		ND		0.004	0.010	0.008
(Terrebonne Co.)		L	6.154	28.529	15.853	0.110	0.357	0.225				0.440	1.316	0.967
Florida	10	W	0.055	0.160	0.096	—	—	<0.005*(5)	0.007	0.011	0.008(7)	<0.006	0.008	—(1)
(Highland Co.)		L	3.924	15.766	8.981	<0.224	<0.505	—(5)	0.519	0.760	0.687(7)	<0.379	0.645	—(1)

W = wet weight; L = lipid weight.
* = All birds reported at this value.
ND = Not detected; value = 0 in computing means.
Numerals in parentheses indicate number of birds in which the compound was not detected.
< quantities taken at face value in computing means.
Means are arithmetic.

TABLE 2.—*Intersite comparison of means of DDE and PCB (ppm lipid basis) in dove breast muscle, 1970-71*[1]

Site		DDE Means			Site		PCB Means		
County	State	Arithmetic	Geometric		County	State	Arithmetic	Geometric	
Oconee	Ga.				Terrebonne	La.	15.85	18.32	a
Toombs	Ga.	9.38	5.45	a	Washington	R.I.	14.13	13.76	ab
Madison	Miss.	7.72	4.67	ab	Cape Girardeau	Mo.	13.32	11.54	abc
Highland	Fla	7.76	4.23	ab	Charleston	S.C.	12.00	11.48	abc
Chocktaw	Ala.				Montgomery	Va.	15.52	11.28	abc
Mobile	Ala.	11.49	3.95	ab	Stewart	Tenn.	12.32	10.84	abc
Cape Girardeau	Mo.	4.98	3.48	abcd	Highland	Fla.	8.98	8.33	bcd
Charleston	S.C.	7.74	3.12	abcd	Chocktaw	Ala.			
Washington	R.I.	3.07	2.82	abcd	Mobile	Ala.	6.17	8.33	bcd
Berks	Pa.	6.00	1.70	abcde	Trigg	Ky.	8.33	7.86	bcd
Trigg	Ky.	0.90	1.12	bcde	Madison	Miss.	8.04	7.48	bcd
Stewart	Tenn.	1.78	1.07	bcde	Oconee	Ga.			
Conway	Ark.	1.73	0.96	cde	Toombs	Ga.	7.43	7.09	bcd
Terebonne	La.	1.06	0.91	de	Conway	Ark.	7.20	6.80	bcd
Wake	N.C.	1.09	0.90	de	Anne Arundel	Md.			
Anne Arundel	Md.				Price Georges	Md.	5.93	6.02	cd
Prince Georges	Md.	0.96	0.61	e	Wake	N.C.	4.65	4.46	d
Montgomery	Va.	1.47	0.45	e	Becks	Pa.	7.03	3.98	d

[1] The geometric means of any two sites not followed by the same letter are significantly different (Duncan multiple range test).

PESTICIDES IN SOIL

DDT Residues in Soil, Water, and Fauna from New York Apple Orchards [1]

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ABSTRACT

Five commercial apple orchards which had not been sprayed extensively with DDT since approximately 1960 were surveyed in 1972 for residues of DDT and its metabolites. In addition to the parent compound, DDE and DDD were almost always recovered, but no dicofol was detected in any soil sample. Total residues in the top 6-in. soil layer underneath the trees ranged from 21.8 to 259 lb/acre. Between the rows of trees the levels were considerably lower; they ranged from 7.3 to 78.5 lb/6-in. acre. In one heavily contaminated orchard, researchers also analyzed stream water, stream-bottom mud, and animals. Very low amounts of DDT (0.32 ppb) and DDD (0.042 ppb) were found in the water, and residues in stream-bottom mud totaled less than 1 ppm. Worms, slugs, snails, tadpoles, fingerling fish, and frogs all contained DDT, DDE, and DDD.

Introduction

Residues of DDT and its metabolites persist in many corners of our environment, but one of the largest reservoirs for these chemicals is orchard soil (*1*). A recent survey which included orchards across the United States revealed a DDT soil load ranging from 0.07 to 245.4 ppm (*2*). Other, less extensive orchard surveys in the United States, Canada, and Great Britain have indicated residue levels somewhere between these extremes (*3-11*). In two of these studies, (*4, 7*), residues of DDT and analogs were also reported for soil insects, slugs, snails, and worms. Most of the animals had accumulated 2 to 4 times as much DDT as was present in their surrounding soil.

In New York, about 72,000 acres of land are currently devoted to commercial apple orchards. Although most of the orchards have not been treated regularly with DDT for more than 10 years, almost all of them had relied on DDT for insect control from approximately 1947 to 1960. During this time, an acre in a typical commercial apple orchard would have been sprayed with 250-400 lb of DDT. The following study was designed to examine how much DDT and metabolites still remained in the soil, how the residue was distributed in the soil, and whether any of the residue had moved into waterways or animal life within the orchard.

Materials and Methods

Five commercial orchards were chosen at random from the heart of New York's apple belt along the southern shore of Lake Ontario. Soil samples were removed from an area near the middle of each orchard. Four of the locations contained trees at least 25 years old, but the trees from orchard G were estimated to be only about 15 years old. Orchard D was sampled in two locations: one at the top of a hill near a stream meandering through the orchard, and the other in a low spot where drainage tile had recently been installed.

At each site, four soil cores were removed from under each of six trees in an area about halfway between the trunk and outer branches. An additional 24 cores were taken from the aisles between the rows of trees. No attempt was made to scrape away surface vegetation or decaying plant debris before sampling. This material was included as part of the upper soil layer. Each cylindrical core consisted of three soil plugs 1⅝ in. in diameter, 2 in. long, and 4.14 cubic in. in volume. After removal of the 2-in. plug, a second sampler was carefully inserted into the same hole to get the 2- to 4-in. plug;

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the same procedure was repeated for the 4- to 6-in. plug. The 24 plugs from each depth were sealed in a plastic bag until they could be weighed and thoroughly mixed. Only large stones were removed to prevent breakage of glassware during the extraction procedure. Since orchard management (cultivation, vegetative cover, etc.) and soil type and texture varied, it was decided to use unscreened wet soil directly from the orchard and to convert all results to lb residue/2-in. acre for comparative purposes.

Two 100-g subsamples from each bag of soil were weighed separately into 1-liter flasks. Enough water (~40 ml) was added to each flask to make a slurry; into the slurry was poured 600 ml of 3:1 petroleum ether: isopropanol. The flask was placed on a wrist-action shaker and thoroughly agitated for 5 min. After separation, the solvent layer was decanted into a 1-liter separatory funnel and the alcohol was removed with three 150-ml washes of water. The remaining petroleum ether extract was dried over anhydrous sodium sulfate and a portion was injected directly into an Aerograph Hy-Fi Model 550-B gas chromatograph equipped with an electron-capture detector and a 3-ft-by-⅛-in-column containing 5% Dow 11 on 60-80 Gas Chrom-Q at a temperature of 195°C. Recovery from DDT-spiked soil samples averaged 95% and method sensitivity allowed for detection levels above 0.13 lb 2-in. acre. Several other extraction procedures were tried, but none removed more residues than did the method described above. There were no chemicals extracted from the soil which interfered with DDT and DDT-analog peaks from the gas chromatograph. Reported values for soil residues have not been corrected for recevorey and represent an average of the two subsamples.

On several occasions, two 1-gal. water samples and two 1-qt bottom mud samples were taken from the stream in orchard D at four different locations. Additional samples were removed from a small bay in the stream where spray tanks were filled and from the end of a drainage tile where it emptied into the stream. The mud samples were extracted as described for soil except that the petroleum ether extract was concentrated before gas chromatography (95% recovery, 0.005 ppm sensitivity limit). Each gallon of water was distributed equally between three 2-liter separatory funnels. To the first funnel was added 150 ml of petroleum ether. After thorough mixing and separation of layers, the petroleum ether was drawn off and transferred to the second funnel. Following extraction of this water, the process was repeated on the third funnel. The entire procedure was reenacted two more times, changing only the sequence of funnels. The combined petroleum ether extracts were dried with anhydrous sodium sulfate and concentrated before gas chromatographic analysis. Spiked recoveries averaged over 98% and method sensitivity was 0.13 ppb.

Orchard D was also the site of animal collections. Worms were obtained by digging soil and turning over surface debris under and between rows of trees in the area where soil samples were removed. Most of the slugs were captured under trees near the stream. Frogs, tadpoles, fingerling fish, and snails were scooped from the stream with a long-handled net. All specimens were brought back to the laboratory where they were washed, weighed, and immediately frozen. This procedure was repeated on two separate occasions, producing a total sample weight of 36.6 g worms, 6.1 g slugs, 107 g frogs, 23.4 g tadpoles, 7.7 g fish, and 11.0 g snails. Each collection was analyzed separately, and results were averaged for the two corresponding samples. Residues were determined after the animals had been freeze-dried and extracted according to the method of Harence et al. (*12*). The final hexane extract was analyzed by gas chromatography as described for soil samples. Recovery from spiked tissues averaged 78% and reported values have been corrected to 100%.

Results and Discussion

All soil samples removed from the orchards contained measurable amounts of DDT and DDE; many samples also contained DDD. Although the analysis procedure allowed for detection of dicofol, which has been discovered in other orchard soil (*8-10*), this DDT metabolite was not picked up in any of the test orchards. The total load of DDT, DDE, and DDD in the top 6 in. of soil and vegetation varied considerably from a high of 258.8 lb/acre under the trees in orchard D to a low of 7.3 lb/acre between the rows of trees in orchard G (Table 1). It is difficult to explain this broad range because the complete spray history of each orchard is unknown. Except for orchard G, the orchards were sampled in areas which had probably been exposed to regular DDT treatments for more than 10 years. Undoubtedly, some of the variation was due to differences in soil type, soil structure, chemical makeup, physical conditions, and cultivation practices. However, only a very small portion of the residues are probably due to the DDT spray used occasionally after 1960 because the total application during this period probably did not amount to more than 2-3 lb/acre.

Based on previous studies, the horizontal and vertical distribution of residues within the soil was not surprising. For example, more residues were located under the trees than between the rows of trees (Table 1). This has been an almost universal finding in orchard surveys (*5, 6, 9, 13, 14*). With the exception of the tiled region between the trees of orchard D, there was a general trend of decreasing contamination with increasing soil depth. A change in residue profile for the tiled region was probably due to the turnover and mixing of soil that occurred when the drainage system was installed. In highly contaminated orchards (D-Hill, C, and P),

75-85% of the total residue still remained in the top 2-in. layer. In the other orchards these values were inclusive for the upper 4 in. of soil. Previous orchard surveys which probed deeper than 6 in. have yielded similar results (*6, 10, 14*), although in these instances samples were taken during or shortly after DDT treatment. The results in Table 1, obtained from orchards that had not been sprayed regularly with DDT for approximately 13 years, indicate that there has been very little downward movement of DDT during this time.

If the total residue distribution is broken down into individual compounds, an interesting consistent observation can be made. At almost every site, the percentage of the total 6-in. residue found in the top 2 in. of soil was nearly the same for DDT and DDE. On the other hand, where DDD was present, its distribution within the top 2 of 6 in. was almost always relatively higher. This higher soil load of DDD in the upper layer is probably due, in part, to several factors. First, during the time of DDT usage, most orchard owners applied some DDD (Rhothane) to control red-banded leaf rollers; infestations of this insect varied greatly from season to season and from orchard to orchard, and the use of DDD varied accordingly. The initial deposition of DDD may have migrated more slowly down into the 4- and 6-in. soil layers than did the DDT. Secondly, microorganisms in the decaying vegetation present in the top soil layer may have converted more DDT to DDD. Orchard sites which contained no detectable levels of DDD could have experienced a minimum amount of DDT-to-DDD conversion in the soil, coupled with a minimum application of DDD.

Of the total residue located in all the orchards at every soil depth, 70-90% persisted as DDT. With some exceptions, the remainder was divided between DDE and DDD so that DDE levels were always approximately equal to or greater than DDD levels. This distribution fits a pattern that seems common to many orchards (*5, 8-10, 15*).

Turning to the animal life collected from orchard D, it is apparent that residues of DDT, DDE, and DDD were present in every species captured (Table 2). Worms and slugs which were in direct contact with the heavily

TABLE 1.—*Residues of DDT, DDD, and DDE in soil from five New York apple orchards*

Soil Level, in.	Residues Expressed as lb/2-in. Acre [1]							
	Under Trees				Between Rows of Trees			
	DDT	DDD	DDE	Total	DDT	DDD	DDE	Total
ORCHARD D, TILED REGION								
0-2	152.0	8.9	14.4	175.3	16.4	4.2	2.1	22.7
2-4	38.3	0.3	4.5	43.1	16.2	0.9	3.4	20.5
4-6	35.7	0.7	4.0	40.4	24.0	4.9	6.4	35.3
0-6	226.0	9.9	22.9	258.8	56.6	10.0	11.9	78.5
ORCHARD D, HILL REGION								
0-2	162.0	14.4	12.3	188.7	40.9	3.0	6.7	50.6
2-4	27.5	1.1	3.4	32.0	6.5	0.3	1.4	8.2
4-6	13.7	1.5	1.9	17.1	3.0	0.1	0.4	3.5
0-6	203.2	17.0	17.6	237.8	50.4	3.4	8.5	62.3
ORCHARD C								
0-2	135.0	19.5	9.7	164.2	42.7	8.5	10.2	61.4
2-4	15.8	0.5	1.4	17.7	9.1	1.2	2.0	12.3
4-6	9.1	0.0	1.1	10.2	2.5	0.0	0.7	3.2
0-6	159.9	20.0	12.2	192.1	54.3	9.7	12.9	76.9
ORCHARD P								
0-2	40.6	0.0	9.4	50.0	22.7	0.0	8.8	31.5
2-4	17.4	0.0	5.0	22.4	5.5	0.0	2.3	7.8
4-6	15.2	0.0	2.6	17.8	1.8	0.0	0.6	2.4
0-6	73.2	0.0	17.0	90.2	30.0	0.0	11.7	41.7
ORCHARD Y								
0-2	17.4	3.0	4.4	24.8	8.2	0.0	3.8	12.0
2-4	10.0	1.2	3.1	14.3	10.6	0.0	4.1	14.7
4-6	5.8	0.0	1.6	7.4	4.0	0.0	1.8	5.8
0-6	33.2	4.2	9.1	46.5	22.8	0.0	9.7	32.5
ORCHARD G								
0-2	8.4	0.6	1.6	10.6	3.2	0.0	0.7	3.9
2-4	6.1	0.0	1.1	7.2	1.4	0.0	0.6	2.0
4-6	3.6	0.0	0.4	4.0	0.9	0.0	0.5	1.4
0-6	18.1	0.6	3.1	21.8	5.5	0.0	1.8	7.3

[1] To convert values for individual 2-in. soil layers to approximate ppm wet weight, multiply by 1.5.

TABLE 2.—*Residues of DDT, DDD, and DDE in animals collected from Orchard D*

Animal	Residues in ppm Based on Wet-weight				Residues in ppm Based on Dry-weight			
	DDT	DDD	DDE	Total	DDT	DDD	DDE	Total
Earthworm	21.7	4.0	5.1	30.8	106	17.6	24.0	147.6
Slug	5.6	5.2	2.6	13.4	28.1	23.9	12.1	64.1
Frog	2.8	1.8	2.2	6.8	13.3	10.0	10.9	34.2
Tadpole	1.7	1.0	0.6	3.3	16.5	9.0	5.1	30.6
Fish	0.5	0.5	0.6	1.6	3.1	3.0	3.8	9.9
Snail	0.8	0.5	0.3	1.6	1.8	1.5	0.7	4.0

contaminated soil in the hill region of orchard D contained the largest quantities of residues on a wet-weight basis. However, the amounts did not approach those found in the upper 6 in. of soil. Other studies have shown that worm and slug residues were considerably higher than surrounding soil residues (*4, 7*), although in such instances the soil load was much less than that of orchard D.

Fittingly, an intermediate contamination level was found in frogs. These animals were exposed to residues on land and in the orchard's small stream. Finally, fingerling fish, tadpoles, and snails contained relatively small quantities of DDT, DDE, and DDD. Unlike the land inhabitants, however, the stream dwellers obviously were capable of concentrating residues from their surroundings. Although none of the water collected contained measurable amounts of DDE, an average of 0.32 ppb of DDT and 0.042 ppb of DDD was found in stream samples. Contamination was slightly higher in water collected from the stream bay and the drainage tile. The increase in the tile water may have resulted from its intimate contact with soil residues as it percolated slowly through the soil column. Interestingly, there was a general increase in the quantity of residues present in water as the season progressed from early spring to early fall. There are several possible reasons for this: e.g., changes in flow rate, volume of flow, contribution from ground water. Contamination of the mud below the stream was considerably higher than that in the water; average residues were 0.08 ppm DDT, 0.06 ppm DDE, and 0.12 ppm DDD. This very low presence of DDT and analogs in water and their concentration in bottom mud and aquatic animal life has been well documented by other studies (*1*).

One noticeable difference between soil residues and animal residues was in the respective amounts of DDT and its degradation products. Only 30-50% of the total contamination in animals was due to DDT itself; in soil, the parent compound represented 70-90% of the total residue. The larger proportion of DDE and DDD in animals was probably due to an increase in DDT metabolism by the animals.

Other investigations have shown that plants grown on DDT-rich soil tend to accumulate DDT residues, although not to the extent of animal life (*1*). A small sample of dandelions was removed from under the trees of orchard D and thoroughly washed with distilled water. Following aqueous homogenization of a 100-g sample, the plants were extracted and analyzed using the same method described for soil samples. Residues on a wet-weight basis were 4.2 ppm DDT, 2.6 ppm DDD, and 0.86 ppm DDE.

Conclusions

Despite the fact that commercial apple orchards in upstate New York have not received regular DDT treatments for about 13 years, their soil is still contaminated with DDT and some of its metabolites. Qualitative estimates and calculated guesswork indicate that, in one particular orchard, approximately half the DDT applied from 1947 to 1960 continues to persist in the soil as DDT, DDD, and DDE. However, results suggest that other orchard soils contain considerably less material even though they were probably all originally exposed to similar spray schedules.

Within one heavily residued orchard, DDT and analogs were detected in all animal species captured and in a small sample of growing vegetation. Many of these animals had been removed from a stream which trickled through the heart of the orchard. Samples of stream water and bottom mud contained minute quantities of DDT residues, implying that movement of the insecticide from the soil into the waterway was not excessive. In fact, the low levels present in the stream environment coupled with the high soil load suggests that the DDT residues are present in a relatively static situation, moved about primarily by animal life and redistributed principally as part of a mobile food chain.

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GENERAL

Chlorinated Insecticide Residues in Kentucky Burley Tobacco: Crop Years 1963-72 [1]

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ABSTRACT

Kentucky Burley tobacco representing crop years 1963-70 was sampled from the storage facilities of the Burley Tobacco Growers Cooperative Association and from auction warehouses in Kentucky in 1968-72. Analyses of these samples in 1972 showed 100% contained DDT-TDE; 96%, dieldrin; 31%, endrin; and 4%, toxaphene. Endosulfan residues were first detected in a few samples of the 1968 tobacco but were present in 100% of the 1970 and 1972 tobacco, and in 83% of the 1971 crop. Average total chlorinated insecticide residues in tobacco produced during 1963-65 were approximately 20 ppm, and for that produced during 1966-69, levels were about 50 ppm. Levels dropped markedly in 1970 to 12 ppm, declined to 9 ppm in 1971, and then to 4 ppm in 1972. During the years when residues were highest, DDT-TDE constituted over 90% of the total, but declined so rapidly after 1968 that they accounted for only 8% of the total chlorinated insecticide residues in the 1972 tobacco; 90% of the residues on the 1972 tobacco was endosulfan. The relationships of area and year of production to the levels of chlorinated insecticide residues on Burley tobacco are discussed.

Introduction

As of this printing, no official pesticide tolerances on tobacco have been established by the U.S. Government. Whether this situation will change is uncertain. However, it is likely that some action will be taken to control the levels of pesticides on future tobacco crops, either by establishing tolerances or by limiting the kinds and/or amounts of chemicals which may be used. The latter control already applies to DDT and TDE; their registration for use on tobacco was cancelled prior to the 1970 growing season.

The future of pesticide tolerances on tobacco may be elucidated to some degree by examining recent action of the West German Government (*1*). Legislation is pending which would place tolerances on approximately 80 different pesticides used on tobacco. Certain chemicals, including the chlorinated insecticides dieldrin, endrin, chlordane, and heptachlor, could not be present at any level, and thus could not be used in any manner for the control of tobacco pests. Other residues would be allowed at low levels, as exist in general environmental contamination, for example. But the acceptable quantities are so low that their use as a pesticide on tobacco probably would be prohibited. Examples of common chlorinated insecticides and their proposed tolerances are DDT-TDE and analogs, 0.1 ppm; toxaphene, 0.1 ppm; and endosulfan, 0.5 ppm.

For most other insecticides commonly used on tobacco the tolerances are usually below 1.0 ppm. However, the tolerance for carbaryl, a carbamate, is 2.5 ppm and for malathion, an organophosphorus compound, it is 3.0 ppm. Although the legislation has not been passed by the West German Government it is quite possible that the final tolerances will remain just this stringent.

Much of the tobacco produced in the United States contains levels of pesticide residues which would not conform to the pending regulations mentioned above. Several studies (*2, 3, 4*) have shown that tobacco of commerical cigarettes contains residues of chlorinated insecticides much greater than the tolerances proposed in West Germany.

A comprehensive study of the chlorinated insecticide content of Kentucky Burley tobacco has not been made;

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its contribution to the residue levels in United States tobacco products is not known. The current study was conducted to determine the levels of chlorinated insecticides in Kentucky Burley tobacco produced in previous years but still available for sale, and to evaluate the effect of changing insecticide use on the levels and kinds of insecticides in tobacco. These factors were studied in relation to grades of tobacco and to areas in which the tobacco was grown.

Methods and Materials

Burley tobacco samples were collected from tobacco held in storage by the Burley Tobacco Growers Cooperative Association (Burley Tobacco Pool) and from auction warehouses in Kentucky. Tobacco in the Burley Tobacco Pool represents many crop years since it is purchased annually by the Federal Government as part of the U.S. Department of Agriculture price control program. This tobacco, still for sale, is stored at various locations in Kentucky and the storage site generally contains crops produced only in that area. It was possible, then, to compare residue levels with the location of crop production for 1963 through 1970, those crop years for which tobacco was available from the Burley Tobacco Pool. This was evaluated in greater detail in studies in which Burley tobacco was taken from the auction markets at the end of the growing seasons in 1968 through 1972.

SAMPLING

Burley Tobacco Pool

Tobacco stored in the Burley Tobacco Pool is in the hand form contained in a hogshead filled with approximately 1000 pounds of tobacco. Because tobacco in one hogshead could be from various farms subjected to diverse insecticides, a sampling method was developed that would yield a small portion of tobacco containing residues representative of the entire hogshead of tobacco.

A 1-in.-by-48-in. core of tobacco was taken from each hogshead at a point 12 inches from the outer edge of the upright container. Analysis of a thoroughly mixed sample collected in this manner gave results comparable to those obtained by analyzing 100 10-g subsamples from a hogshead of tobacco which has been chopped and mixed by commercial means (*5*).

Four different storage sites in Kentucky were selected for sampling, one each in areas II, III, IV, and V (Fig. 1). The specific warehouses were selected because they contained tobacco produced in that area, and because of the large number of crop years for which tobacco was available. When possible, three different grades of tobacco from each crop year were collected from each sampling site. The grades preferred were B3F, C4F, and X3F because they contain leaves approximating the top, middle, and bottom portions of the tobacco plant. When these grades were not available, similar grades were sampled; in some cases, similar grades were not available so no sample was taken.

For crop years 1965 and 1967-70, 2 hogsheads of each grade were sampled from areas II-V, making a total of 8 hogsheads per grade per year. Grade B, 1963 tobacco was not available in areas III, IV, and V; nor were B and C grades of the 1964 crop in area III. Sampling of the 1966 crop was complete except that there was no grade B tobacco in area II. Two core samples were taken from each hogshead; the tobacco from each was cut into cigarette-size particles and thoroughly mixed. Two 10-g subsamples from each core were analyzed.

Auction Warehouse Tobacco

For sampling purposes, Kentucky was divided into six areas (Fig. 1) and tobacco was collected from as many counties and individual farms within the area as were available at the time of collection. Three hands of tobacco from each farm were collected: one hand each from the top, middle, and bottom leaves of the tobacco plant. A composite sample also was taken which consisted of equal quantities of the top, middle, and bottom leaves. The four samples were individually cut into cigarette-size particles, combined with like samples from the same area, and thoroughly mixed. Two 10-g subsamples were removed for analysis. The numbers of counties and farms represented for each area and crop year are shown in Figure 1. Separate analyses were performed on the top, middle, bottom, and composite leaves from each area for the crop years 1968-72.

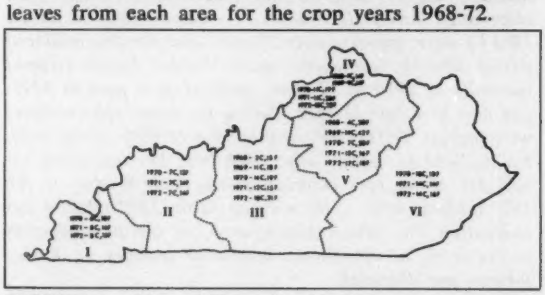

FIGURE 1.—*Map of Kentucky showing areas from which tobacco samples were taken, and number of counties (C), and farms (F) represented by auction warehouse samples for indicated crop years.*

All analyses were performed during 1972 and early 1973 using identical procedures for all samples. Tobacco from the Burley Tobacco Pool was stored in hogsheads, as stated earlier; tobacco samples collected annually from the auction markets were placed in plastic bags and held in the laboratory until analyzed.

Extraction and Cleanup

Tobacco samples were extracted overnight in a soxhlet apparatus with a 9:1 mixture of chloroform and methanol (*6*). Florisil column cleanup of the extracts

for analysis of all chlorinated insecticides except endosulfan was identical to that described by Skrentny and Dorough (*7*). A deactivated florisil column, 2% water, was used for extracts being analyzed for endosulfan (*4*).

Gas Chromatography

Two Varian Aerograph Model 1700 instruments equipped with tritium electron capture detectors were used in these experiments. One chromatograph contained a 6 ft.-by-⅛-in. pyrex column packed with a 1:1 mixture of 4% SE30 and 6% QF1 on 80/90-mesh Anakrom ABS. The temperatures of the injector, column, and detector were 215°C, 200°C, and 210°C. A column of the same size containing 5% OV-210 on 100/200-mesh Chromosorb W-HP was used with the other instrument. The injector temperature was 210°C, the column was 180°C, and the detector was 210°C. Nitrogen, 40 ml/min, served as the carrier gas for both instruments.

Chromatograms of the various insecticide standards and tobacco extracts obtained with these gas chromatographic systems are illustrated in the paper by Dorough and Gibson (*4*). Minimum detectable levels of the insecticides in tobacco were 0.01 ppm for *p,p'*-DDT, *o,p*-DDT, *p,p'*-TDE, *o,p*-TDE, *p,p'*-DDE, dieldrin, endrin, chlordane, endosulfan I and II; 0.05 for endosulfan sulfate; and 0.5 ppm for toxaphene. Average recoveries of the insecticides when added to control tobacco exceeded 90% for all materials except endosulfan sulfate and toxaphene; recoveries of these insecticides averaged 88 and 80%, respectively. The extraction procedure reported here removed from 25 to 80% more chlorinated insecticide residues from tobacco than did certain other extraction methods commonly employed (*7*). Data were not corrected for recovery. Mass spectrometry (Finnigan Model 1015C GC/MS System) was used to confirm the findings.

Results and Discussion

FREQUENCY OF OCCURRENCE

DDT and/or TDE residues were present at detectable levels in all tobacco samples analyzed in this study (Table 1). During the period from 1963 to 1969, all samples except some of the 1964 tobacco crop contained residues in excess of 5 ppm and many contained over 25 ppm of DDT-TDE. Over 80% of the tobacco produced in 1966-69 contained DDT-TDE residues in excess of 25 ppm, but in the 1971 crop the residues were less than 5 ppm in 50% of the samples. DDT-TDE residues on the 1972 crop were below 1 ppm.

Dieldrin also was present on most of the tobacco sampled from the Burley Tobacco Pool and from the auction warehouses. Among samples from the 1964 and 1970 tobacco crops, 90% and 96% contained dieldrin. All other samples from the Burley Tobacco Pool were contaminated with this insecticide. All tobacco collected from the auction warehouses contained dieldrin up to the 1972 crop, in which 33% of the samples were free of detectable levels of residues.

Endrin was the third most common chlorinated insecticide on tobacco: only the 1968 and 1969 auction market samples did not show endrin residues at some level. Unlike dieldrin, endrin was not detected in 100% of the samples for any crop produced between 1963 and 1972. Usually, less than half the samples analyzed for any given crop year contained this material. Also, the

TABLE 1.—*Frequency of occurrence of chlorinated insecticide residues in Kentucky Burley tobacco.*

Crop Year	Percent of samples containing							
					Total DDT-TDE			
	Toxaphene	Endosulfan	Dieldrin	Endrin	0-1 ppm	1-5 ppm	5-25 ppm	25+ ppm
BURLEY TOBACCO POOL SAMPLES								
1963	17	0	100	72	0	0	100	0
1964	0	0	90	60	0	25	40	35
1965	4	0	100	29	0	0	71	29
1966	4	0	100	45	0	0	9	91
1967	0	0	100	21	0	0	17	83
1968	0	0	100	25	0	0	13	87
1969	8	96	100	30	0	0	4	96
1970	8	100	96	17	33	50	17	0
AUCTION WAREHOUSE SAMPLES								
1968	0	35	100	0	0	0	0	100
1969	0	35	100	0	0	0	0	100
1970	17	100	100	17	0	60	33	7
1971 [1]	0	83	100	50	50	17	33	0
1972	0	100	67	33	100	0	0	0

[1] 83% of these samples also contained chlordane.

occurrence of endrin on tobacco was not evenly distributed across the state as were DDT and dieldrin residues. For example, of the 64 hogsheads containing endrin-contaminated tobacco (a total of 180 were sampled for 1963-70), 39 were in area II; 13, in area III; 5, in area IV; and 7, in area V (Fig. 1). Areas I and VI were not included in the Burley Tobacco Pool experiments because of the relatively low quantities of tobacco produced in these areas.

Toxaphene was not a general contaminant of tobacco produced in Kentucky during 1963-72, but did occur sporadically and sometimes at very high levels. Residues of toxaphene were not detected on any samples of tobacco collected from areas IV, V, and VI. Low levels of chlordane were present on 83% of the auction warehouse samples collected in 1971 but none was detected in any other tobacco samples.

Endosulfan residues appeared on about one third of the tobacco sampled from the auction markets in 1968 and 1969. In subsequent years endosulfan was a general contaminant, present in all 1970 and 1972 samples and in 83% of the 1971 auction warehouse tobacco. Its high rate of occurrence on Burley tobacco produced after 1968 was verified by analysis of the Burley Tobacco Pool samples.

Table 1 shows some differences in the frequency with which insecticides occurred on the Burley Tobacco Pool compared to samples from the auction warehouses for the same crop year. These differences become even more apparent in later discussions which consider specific levels. Generally, the Burley Tobacco Pool samples would more accurately represent average residue levels for a given area, or for the State as a whole. This is because a single hogshead of tobacco may contain tobacco produced by as many as 20 farmers at any location within any designated area.

For most crop years from 1963 to 1970, 8 hogsheads were sampled from each area. This would represent tobacco from 100 to 200 producers from that area each year and the resulting data would be indicative of the residues for the area as a whole.

On the other hand, samples from the auction markets were taken from three or four specific warehouses within an area, usually representing crops produced by only 10 to 20 farmers for each area and crop year. Moreover, areas I and VI (Fig. 1) were included in the auction warehouse studies and information from these areas are included in all data reflecting average residue levels on tobacco on a statewide basis (Tables 1, 3, 7, 9). Similar data from the Burley Tobacco Pool samples (Tables 1, 2, 6, 8) would not include tobacco from areas I and VI. These factors could certainly be responsible, at least in part, for the differences observed in insecticide occurrence and levels on tobacco samples taken from the Burley Tobacco Pool and the auction warehouses for the same crop years, although the differences were not dramatic.

TOTAL CHLORINATED INSECTICIDE RESIDUES ON STATEWIDE BASIS

The average levels of chlorinated insecticide residues on Burley tobacco produced in Kentucky during 1963-72 were of three definite magnitudes. Tobacco crops produced in 1963-65 contained average residues of 20 ppm; tobacco produced in 1966-69, about 50 ppm; and that produced after 1969, less than 15 ppm (Tables 2, 3). Total chlorinated insecticide residues continued to

TABLE 2.—*Chlorinated insecticide residues, ppm, in tobacco sampled from Kentucky Burley Tobacco Pool*[1]

Crop Year	Total DDT-TDE's	Dieldrin	Endrin	Endosulfan	Toxaphene	Total Residues
1963	12.26	0.40	0.36	0	7.53	20.55
1964	20.06	0.32	0.30	0	0	20.68
1965	25.55	0.46	0.22	0	0.28	26.51
1966	52.99	0.84	0.25	0	0.67	54.75
1967	50.62	0.70	0.19	0	0	51.51
1968	50.96	0.84	0.14	0	0	51.95
1969	53.02	0.86	0.28	0.86	0.68	55.70
1970	3.54	0.26	0.06	2.68	1.92	8.46

[1] Values are averages of analyses of all hogsheads sampled for indicated year. Number of hogsheads sampled: 18 in 1963, 20 in 1964, 22 in 1966, and 24 in 1965 and 1967-70.

TABLE 3.—*Chlorinated insecticide residues, ppm, in Burley tobacco sampled from auction warehouses in Kentucky*[1]

Crop Year	Total DDT-TDE's	Chlordane	Dieldrin	Endrin	Endosulfan	Toxaphene	Total Residues
1968	54.68	0	0.61	0	0.23	0	55.52
1969	53.24	0	0.94	0	0.30	1.62	56.10
1970	8.16	0	0.59	0.07	4.19	1.14	14.15
1971	3.18	0.27	0.12	0.12	4.60	0.46	8.75
1972	0.29	0	0.04	0.06	4.10	0	4.49

[1] Values are averages of all analysis of samples collected for indicated year.

decline steadily after the very significant drop which occurred in the 1970 tobacco crop, averaging less than 5 ppm in 1972 (Table 3). DDT-TDE constituted over 90% of the total chlorinated insecticide residues on tobacco when residues were at their peak level during 1966-69. The decline in later years was brought about largely by a reduction in levels of these residues. The most significant point was the low level to which they declined: from 53 ppm in 1969, to 0.3 ppm in 1972. Dieldrin residues on Burley tobacco ranged from 0.26 to 0.94 ppm on a statewide basis in the 1963-70 tobacco crops (Tables 2, 3). The average level during this period for tobacco sampled from the Burley Tobacco Pool was 0.60 ppm (Table 2). Endrin levels on the 1963-65 tobacco, 0.2-0.4 ppm, were approximately equal to those of dieldrin. However, endrin residues remained about the same through 1969, whereas levels of dieldrin increased during the late sixties.

Analysis of the 1968 and 1969 auction market samples did not reveal any endrin residues, but low levels were present on the 1970-72 tobacco (Table 3). Like the DDT-TDE's, levels of dieldrin and endrin steadily decline on tobacco produced after 1969; the average level of dieldrin and endrin on the 1972 crop was 0.04 ppm and 0.06 ppm, respectively.

As stated earlier, toxaphene was not present on a large number of samples. However, some individual samples contained more than 100 ppm of this insecticide, causing its levels in tobacco, considered statewide, to appear significant in some cases (Table 2). The toxaphene residues shown in Table 2 were in tobacco from only 9 of the 180 hogsheads sampled: 4 from area II, and 5 from area III. Therefore, toxaphene was not a general contaminant of Kentucky Burley tobacco, nor of tobacco in areas II and III. No toxaphene was detected in 79 of the 88 hogsheads from these areas.

Endosulfan first appeared on the 1968 tobacco crop, but on a statewide basis averaged only 0.23 ppm (Table 3). In 1969, the levels remained fairly low, less than 1 ppm (Tables 2, 3), but increased markedly to over 4 ppm in the 1970-72 Burley tobacco (Table 3). Its

TABLE 4.—*Chlorinated insecticide residues, ppm, in tobacco sampled from Kentucky Burley Tobacco Pool according to area of production and crop year*

Area, Year	*p,p'*-DDT	*o,p*-DDT	*p,p'*-TDE	*o,p*-TDE	*p,p'*-DDE	Total DDT-TDE	Endosulfan	Dieldrin	Endrin	Toxaphene	Total Residues
Area II											
1963	3.16	0.93	6.17	1.45	0.40	12.11	0	0.68	0.83	29.32	42.93
1964	5.57	0.71	15.78	4.13	0.66	26.85	0	0.55	0.96	0	28.36
1965	9.94	1.14	28.96	8.71	0.80	49.54	0	1.03	0.84	0	51.42
1966	27.55	2.72	34.60	10.13	1.63	76.64	0	1.26	0.96	0	78.86
1967	32.11	3.15	39.29	7.31	2.15	84.02	0	1.39	0.75	0	86.16
1968	19.22	1.91	41.14	7.02	1.70	70.99	0	1.47	0.50	0	72.96
1969	24.06	2.28	45.84	8.93	1.60	80.71	0.94	1.22	1.05	0	83.92
1970	1.48	0.18	3.12	1.81	0.14	6.74	3.40	0.31	0.25	7.68	18.37
Area III											
1963	1.39	0.19	9.15	1.74	0.14	12.61	0	0.22	0.61	0.81	14.24
1964	5.62	0.90	13.44	2.90	0.64	23.51	0	0.36	0.20	0	24.07
1965	5.45	0.77	12.21	2.61	0.54	21.58	0	0.34	0.02	1.10	23.05
1966	31.68	2.78	24.16	4.34	1.98	64.94	0	0.68	0.02	2.68	68.32
1967	15.36	1.68	26.04	6.01	1.33	50.42	0	0.62	0	0	51.04
1968	16.97	1.64	22.07	4.21	0.88	45.77	0	0.65	0.10	0	46.52
1969	17.64	2.04	32.47	8.50	1.34	62.00	0.88	1.09	0.05	2.70	66.71
1970	1.68	0.22	1.41	0.35	0.07	3.74	3.04	0.26	0.01	0	7.04
Area IV											
1963	0.93	0.09	7.83	2.00	0.13	10.97	0	0.31	0.01	0	11.28
1964	7.08	0.79	5.48	1.06	0.78	15.16	0	0.10	0	0	15.26
1965	6.02	0.72	4.79	1.23	0.74	13.50	0	0.19	0	0	13.68
1966	16.67	1.64	16.95	3.90	1.57	40.72	0	0.44	0.01	0	41.17
1967	12.53	1.08	14.68	2.31	1.04	31.64	0	0.21	0	0	31.85
1968	14.15	1.38	12.97	2.72	1.29	32.50	0	0.47	0	0	32.98
1969	14.16	1.45	12.78	2.37	0.99	31.74	0.88	0.52	0	0	33.14
1970	0.17	0.02	1.36	0.34	0.01	1.90	1.40	0.27	0	0	3.56
Area V											
1963	3.16	0.53	7.14	2.11	0.40	13.33	0	0.39	0.02	0	13.74
1964	3.62	0.42	8.13	2.09	0.45	14.72	0	0.27	0.04	0	15.03
1965	3.77	0.47	10.24	2.67	0.44	17.58	0	0.30	0.01	0	17.90
1966	12.28	1.42	12.18	2.93	0.86	29.66	0	1.00	0	0	30.66
1967	9.40	1.11	20.15	4.65	1.11	36.41	0	0.57	0	0	36.98
1968	23.26	2.07	24.56	3.60	1.06	54.56	0	0.78	0	0	55.34
1969	14.38	1.28	18.11	3.16	0.69	37.61	0.76	0.60	0	0	38.98
1970	0.54	0.09	0.77	0.34	0.05	1.80	2.86	0.21	0	0	4.86

ubiquitous nature and the fact that many samples contained 10 to 20 ppm endosulfan is not unlike the situation in the early 1960's regarding DDT-TDE residues on tobacco.

RESIDUES IN RELATION TO AREA OF PRODUCTION AND CROP YEAR

Of the four areas in Kentucky from which Burley Tobacco Pool samples were collected (Fig. 1), the highest levels of total chlorinated insecticide residues were always found in tobacco from area II (Table 4). The average level for the 8-year period was 58 ppm. During 6 of the 8 years, tobacco from area IV contained the lowest quantity of insecticide residues; area V tobacco was lowest the other 2 years. Eight-year averages for areas IV and V were 23 ppm and 27 ppm, respectively. Tobacco from area III always contained residues higher than those from area IV and, except for the 1968 crop, lower than area V. Total chlorinated insecticide residues on area III tobacco averaged 38 ppm for the crop years 1963-70.

Analysis of the auction warehouse tobacco samples showed that area I tobacco was similar in insecticide content to that from area II (Table 5). Area VI tobacco proved to be lower in chlorinated insecticide content than tobacco from any of the areas in which samples were collected in 1970-72. Average total residues were

TABLE 5.—*Chlorinated insecticide residues, ppm, in Burley tobacco sampled from auction warehouses in Kentucky according to area of production and crop year*

Area, Year	*p,p'*-DDT	*o,p*-DDT	*p,p'*-TDE	*o,p*-TDE	*p,p'*-DDE	Total DDT-TDE	Chlordane	Endosulfan	Dieldrin	Endrin	Toxaphene	Total Residues
Area I												
1970	4.29	0.48	8.30	1.54	0.21	14.82	0.00	14.63	2.22	0.00	6.62	38.29
1971	2.73	0.79	5.21	1.21	0.21	10.15	0.15	13.78	0.15	0.55	0	24.78
1972	0.29	0.11	0.10	0	0.03	0.53	0	7.45	0.08	0.07	0	8.13
Area II												
1970	5.12	0.38	23.49	5.37	0.20	34.56	0	3.21	0.71	0.63	0	39.11
1971	1.52	0.40	5.79	1.23	0.09	9.03	0.08	10.85	0.14	0.62	0	20.72
1972	0.20	0.07	0.09	0	0.02	0.38	0	5.46	0.02	0.43	0	6.29
Area III												
1968	1.17	0.56	24.93	4.63	0.07	31.76	0	0	0.73	0	0	32.49
1969	16.14	2.06	39.02	9.97	0.88	68.07	0	0	1.23	0	4.07	73.37
1970	0.24	0.16	1.70	0.39	0	2.49	0	2.28	0.10	0	0	4.87
1971	0.12	0.11	1.27	0.28	0	1.78	0.06	2.81	0.19	0.25	0	5.09
1972	0.19	0.07	0.06	0	0.02	0.34	0	3.65	0	0	0	3.99
Area IV												
1968	35.23	5.32	12.15	0.92	0.71	54.33	0.00	0.00	0.27	0.00	0.00	54.60
1969	14.41	2.16	19.33	4.77	0.97	41.64	0	0	0.99	0	0	42.63
1970	0.22	0.11	0.80	0.29	0	1.42	0	2.93	0.64	0	0	4.99
1971	0.11	0.09	0.13	0.03	0.01	0.37	0.04	0.89	0.07	0	0	1.37
1972	0.08	0.03	0.04	0.01	0.01	0.16	0	2.59	0.07	0	0	2.85
Area V												
1968	16.69	2.89	20.57	3.87	0.95	47.94	0	0.90	0.90	0	0	49.74
1969	19.83	2.19	17.29	2.76	0.83	42.90	0	1.06	0.86	0	0	44.82
1970	2.95	0.69	8.86	1.63	0.09	14.22	0	3.26	0.47	0	0	17.95
1971	0.07	0.05	0.11	0.03	0.01	0.27	0	1.39	0.08	0	0	1.78
1972	0.09	0	0.04	0	0	0.13	0	1.91	0.04	0	0	2.08
Area VI												
1970	0.74	0.17	1.27	0.36	0	2.54	0	0.55	0.05	0	0	3.14
1971	0.05	0.09	0.05	0.01	0	0.16	0.05	0	0.02	0	0	0.25
1972	0.06	0	0.04	0	0	0.10	0	0.12	0	0	0	0.22

TABLE 6.—*Endosulfan components in tobacco sampled from Kentucky Burley Tobacco Pool*

	PPM AND PERCENTAGE OF TOTAL ON TOBACCO FOR CROP YEARS [1]							
	1969				1970			
	Endosulfan				Endosulfan			
Grade	I	II	Sulfate	Total	I	II	Sulfate	Total
B3F	0.10	0.35	0.19	0.64	0.22	1.17	1.12	2.51
C4F	0.08	0.31	0.44	0.83	0.23	1.13	1.30	2.66
X3F	0.14	0.34	0.65	1.13	0.24	1.17	1.32	2.73
Average	0.11 (12.6)	0.33 (37.9)	0.43 (49.5)	0.87	0.23 (8.8)	1.16 (44.1)	1.25 (47.1)	2.63

[1] Values represent average of analysis of tobacco from 8 hogsheads: 2 of each grade each year from each area, II-V, described in Fig. 1.

TABLE 7.—*Endosulfan components on Burley tobacco sampled from auction markets in Kentucky*

Crop Year and Insecticide	PPM and percentage of total on leaves from different portions of plant [1]				
	Top	Middle	Bottom	Average	Composite [2]
1970					
Endosulfan I	0.65	0.80	0.86	0.77 (18.9)	0.78 (17.4)
Endosulfan II	1.13	1.15	1.22	1.17 (28.5)	1.38 (30.8)
E. Sulfate	1.86	2.33	2.30	2.16 (52.6)	2.32 (51.8)
Total	3.64	4.28	4.38	4.10	4.48
1971					
Endosulfan I	0.51	0.88	0.90	0.76 (18.5)	0.80 (16.1)
Endosulfan II	2.51	1.03	1.56	1.70 (41.4)	2.27 (45.8)
E. Sulfate	1.40	1.41	2.15	1.65 (40.1)	1.89 (38.1)
Total	4.42	3.32	4.61	4.11	4.96
1972					
Endosulfan I	0.29	0.31	0.66	0.42 (8.3)	0.25 (7.1)
Endosulfan II	0.79	1.13	2.64	1.52 (16.1)	0.81 (23.0)
E. Sulfate	2.60	3.57	3.12	3.10 (75.6)	2.47 (69.9)
Total	3.68	5.01	6.42	5.04	3.53

[1] Average of all samples analyzed for indicated year.
[2] Sample consisting of equal quantities of top, middle, and bottom leaves.

TABLE 8.—*Chlorinated insecticide residues, ppm, in different grades of tobacco sampled from Kentucky Burley Tobacco Pool*[1]

Crop Year	Grade			Average
	B	C	X	
1963	14.82	37.45	9.38	20.55
1964	29.78	17.83	14.43	20.68
1965	24.88	24.41	30.25	26.51
1966	51.25	59.80	53.20	54.75
1967	55.37	43.66	55.50	51.51
1968	56.34	50.09	49.42	51.95
1969	47.53	48.87	70.70	55.70
1970	8.95	9.59	6.84	8.46
Average	36.12	36.46	36.21	36.26
Years high, %	25	38	38	—
Years medium, %	50	38	12	—
Years low, %	25	25	50	—

[1] Values are averages of analysis of all hogsheads sampled for indicated year: 8 hogsheads/grade/year in 1965 and 1967-70; 8 hogsheads each for grades X and C, 2 for grade B in 1963; 8 hogsheads for grade X and 6 each for grades B and C in 1964; 8 hogsheads each for grades X and C and 6 for grade B in 1966.

TABLE 9.—*Chlorinated insecticide residues, ppm, in tobacco sampled from auction markets in Kentucky according to position of leaves on plant*[1]

Crop Year	Position on plant				ppm on Composite Sample [2]
	Top	Middle	Bottom	Average	
1968	61.08	58.35	57.07	58.83	45.61
1969	48.61	63.10	59.09	56.93	53.61
1970	14.42	17.04	10.46	13.97	18.06
1971	9.92	6.68	9.21	8.66	9.00
1972	4.01	5.32	4.74	4.69	3.92
Average	22.61	30.10	28.11	28.60	26.04
Years high, %	40	60	0	—	—
Years medium, %	20	20	60	—	—
Years low, %	40	20	40	—	—

[1] Values are averages of analysis of all samples analzed for indicated year.
[2] Sample consisting of equal portions of top, middle, and bottom leaves.

only 3.14 ppm in 1970 and below 0.3 ppm in 1971 and 1972. Residues on the 1972 crop from other areas also were much lower than in 1970, especially in areas I and II where total residues averaged over 20 ppm in 1971 but were 8 ppm and 6 ppm, respectively, in 1972.

It was particularly noteworthy that total DDT-TDE residues were so low in all 1972 tobacco (Table 5). These findings eliminated the possibility that the previous use of DDT and/or TDE for many years, and at high rates, would result in significant contamination of subsequent tobacco crops even after these insecticides were discontinued. Tables 4 and 5 show numerous instances in which DDT-TDE residues dropped to 1 ppm or less in tobacco produced in an area where, just the year before, the crop had contained over 20 ppm. This proved to be the case even in area II where the residues were highest each of the past 10 years. In fact, the most dramatic reduction in any single year occurred in area II where total DDT-TDE residues were 80.7 ppm in 1969 and only 6.7 ppm in 1970.

Determining relative concentrations of the individual components comprising the total DDT-TDE residues showed that the ratios of the compounds varied considerably from sample to sample (Tables 4, 5). By averaging the results of all tobacco samples analyzed in this study, it was found that total DDT-TDE residues consisted of 50% *p,p'*-TDE, 30% *p,p'*-DDT, 12% *o,p*-TDE, 6% *o,p*-DDT, and 2% *p,p'*-DDE. Only after total residues on tobacco had declined to the point that minor components could no longer be detected, could a consistent variation from these average values be obtained. This had little meaning, however, since all five components were usually present in samples containing 0.5 ppm, and sometimes less, of either *p,p'*-DDT or *p,p'*-TDE.

Concomitant with the decline of DDT-TDE residues was the increased levels of endosulfan in tobacco. Maximum levels, up to 14 ppm, occurred in tobacco from areas I and II, but generally declined as the area of crop production moved eastward across the State. Area VI tobacco contained 0.55 ppm endosulfan in 1970, none in 1971, and only 0.12 ppm in 1972. Except for areas I and II, higher endosulfan residues were found in the 1972 tobacco than in the 1971 material.

Generally, the levels of dieldrin and endrin varied according to area of production and crop year in much the same manner as the DDT-TDE residues. By 1972, the levels had declined to a point where the highest level of dieldrin in any area was only 0.08 ppm (Table 5) and this occurred in area I. None of the 1972 samples from area III or VI contained dieldrin. Endrin residues of relatively high quantities, 0.43 ppm, were in the 1972 tobacco from area II, but were only 0.07 ppm in area I. All other samples were free of endrin residues in 1972. Of all samples collected from the auction warehouses, toxaphene was detected only in the 1969 area III and the 1970 area I tobacco.

ENDOSULFAN

It was evident from analyses of both the Burley Tobacco Pool and auction warehouse samples that many tobacco producers were using endosulfan as a replacement for DDT and TDE. Residues of endosulfan rose sharply in crops produced after 1969, the last year DDT and TDE were approved for control of tobacco insect pests. Because endosulfan is still approved for use on tobacco and was the predominant chlorinated insecticide residue on the 1971 and 1972 Burley tobacco crops, a more critical evaluation of its residual nature in tobacco is presented in Tables 6 and 7.

Total endosulfan residues consisted of the two isomers of the compound, endosulfan I and II, and endosulfan sulfate. Analysis of the three endosulfans on tobacco leaves from the top (B3F), middle (C4F), and bottom (X3F) of the plant showed that the bottom leaves contained the highest concentrations of total endosulfan residues. Generally, endosulfan residues were somewhat higher in the middle leaves than in the top ones. Although the differences were consistent, the magnitude was usually less than 1 ppm between the top and bottom leaves. Actually, it might be expected that the top leaves would contain the higher level of residues since endosulfan is applied as foliar spray to tobacco. It may be that residues on the lower portion of the plant are protected from weathering by the upper foliage, thus slowing dissipation rates. Another contributing factor could be dilution by growth of the upper leaves when younger plants are sprayed.

In most of the tobacco analyzed, endosulfan sulfate accounted for 40 to 50% of the total endosulfan residues. Endosulfan II constituted 30 to 40% and the remaining 10 to 20% was endosulfan I. The 1972 tobacco crop, however, showed a different pattern (Table 7). Endosulfan sulfate was approximately 70% of the total residues; endosulfan II, about 20%; and endosulfan I, only 8%. Whether this is typical of newly harvested tobacco was not ascertained. However, it is unlikely that these data mean that significant changes in composition of endosulfan residues took place during storage of the 1969-70 tobacco samples. If this were the case, endosulfan sulfate residues should be less in newly harvested samples; they are formed from endosulfan I and II, and this conversion would have more time to occur in the stored tobacco. The fact that the relative concentrations of the endosulfan components were fairly similar on all tobacco suggests that little dissipation and/or conversion of endosulfan residues to other products occurred during storage.

RESIDUES IN RELATION TO GRADE OF TOBACCO

Tobacco stored in hogsheads by the Burley Tobacco Pool is graded before being placed in storage and this information is recorded on each container. Grades B3F, C4F, and X3F were sampled for residue analysis whenever possible because these grades generally represent the top, middle, and bottom leaves of the tobacco plant, respectively.

Samples from the auction warehouses were taken before being graded but the samples were taken based on the position of the leaves on the intact plant. Therefore, it was possible to correlate levels of residues with grades of tobacco in samples taken from the Burley Tobacco Pool and the auction markets.

The 8-year average chlorinated insecticide residue levels on the Burley Tobacco Pool samples were almost identical for all three grades of tobacco (Table 8). During this period, however, grades B and C contained the lowest level of residues only 25% of the time; grade X tobacco was lowest of the three grades 50% of the time. Residues on grades C and X were higher than grade B material 38% of the time. Grade B material was highest 25% of the time. During the years when residues were in the low and/or medium range, grade B tobacco was highest 75% of the time. These data do suggest a trend in regard to residue levels and grades of tobacco, but the differences are so small and inconsistent that it is impossible to consider them of any practical importance.

A similar conclusion may be drawn from data in Table 9 which show residue levels on the top, middle, and bottom leaves of tobacco sampled from auction warehouses. Average residue levels of chlorinated insecticides for crop years 1968 through 1972 were 23 ppm for the top leaves, 30 ppm for the middle leaves, and 28 ppm for the bottom leaves. As expected, these values were

less than the 8-year averages, 36 ppm, for tobacco stored in the Burley Tobacco Pool (Table 8). Calculating the frequency with which residue levels were either high, medium, or low on leaves from different positions of the tobacco plant failed to demonstrate a definite pattern of residue distribution (Table 9). The fact that these data on the auction market samples were different from but as variable as those for the Burley Tobacco Pool samples supports the conclusion that residue levels were independent of grade of tobacco.

Data in Tables 7 and 9 suggest that, for monitoring purposes, a composite sample consisting of equal quantities of top, middle, and bottom leaves would be a valid sample for analysis of the chlorinated insecticides. Actually, a sample taken from any one portion of the plant might serve the same function. However, if the apparent trend toward lower residues on top leaves is real as indicated by the data on endosulfan (Table 7), a composite sample would be of greater value in determining the level of residues on an entire tobacco crop.

It is significant that the findings of this study are limited to the chlorinated insecticides and that the distribution of other pesticides on tobacco could differ significantly. Soil-applied systemic pesticides, in particular, might be different from the chlorinated insecticides investigated in this study. With few exceptions, these latter materials are applied as sprays directly on the plant and contamination is dependent largely on mechanical factors and ambient conditions. Contamination of tobacco by systemic insecticides would normally involve complex interactions of the chemical with various biochemical and physiological processes of the tobacco plant.

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BRIEF

Mercury Levels in Soils of the Eastern United States

G. B. Wiersma[1] and H. Tai[2]

ABSTRACT

Cropland and noncropland soils were sampled to determine levels of elemental mercury present in the upper three inches of soil. Results showed no difference in mercury levels between cropland and noncropland soils. Levels detected compared closely to levels found in similar studies. Actual mean levels of mercury residues in soils of the eastern United States ranged from 0.05 to 0.10 ppm.

Introduction

This study is an effort to determine baseline levels of elemental mercury in cropland and noncropland soils in the eastern United States. These baselines, in turn, will be used for comparison with results from continuing soil monitoring efforts for pesticides containing mercury.

Several estimates have been made of baseline levels of mercury in soils, both in the United States and abroad. Warren and Delavault (*1*) reported very high concentrations of mercury in certain British soils ranging as high as 15 ppm. They estimated, however, that the levels of mercury in most British agricultural soils would probably range between 0.01 and 0.06 ppm. Anderson (*2*) analyzed soils in Sweden and found that ranges for mercury in these soils varied from 0.02 to 0.92 ppm with an average of 0.07 ppm. Sand et al. (*3*) reported mercury residues in wheat-growing areas of the north-central United States.

Pierce et al., (*4*) reported mercury concentrations in soil from four areas in the western United States. The 50 percentile points for these four sets of data ranged from 0.071 ppm to 0.200 ppm. Shacklette et al. (*5*) collected 912 soil samples along widely scattered road systems in the continental United States. Sample sites were approximately 50 miles apart.

Sampling was conducted to the depth of 8 inches. The geometric means for mercury concentration in these soil samples for the entire United States was 0.071 ppm. The arthmetic mean was 0.112 ppm. The geometric mean for the western United States, 492 samples from west of the 97th meridian, was 0.055 ppm; the arithmetic mean was 0.083 ppm. The eastern United States, 420 samples, had a geometric mean of 0.096 ppm and an arithmetic mean of 0.147 ppm.

Material and Methods

Samples were collected as a subset of the National Soils Monitoring Program as described by Wiersma et al. (*6*). Sites were allocated according to the relative amounts of cropland and noncropland acreages in each State. Sites were chosen at random within the two categories. States sampled and the number of sites in each state are listed in Table 1.

At each sampling point a 10-acre site was sampled. Fifty soil cores, 2 inches in diameter by 3 inches deep, were collected and composited with the use of a 5-by-10 grid. A 2-quart subsample was then taken and sent to the laboratory for analysis. The cropland samples were collected in the fall of 1968, along with noncropland samples from Georgia, Maine, Maryland, Virginia, and West Virginia. All other noncropland samples were collected in the spring of 1971.

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TABLE 1.—*Soil samples collected to determine mercury residues in surface cropland and noncropland areas of eastern United States*

State	Number of samples collected	
	Cropland	Noncropland
Alabama	6	6
Arkansas	13	5
Connecticut	1	1
Delaware	1	No samples tested
Florida	5	7
Georgia	8	8
Illinois	41	3
Indiana	22	1
Kentcuky	8	4
Louisiana	8	5
Maine	2	2
Maryland	3	1
Massachusetts	1	1
Michigan	16	*
Mississippi	9	5
Missouri	23	7
New Hampshire	1	1
New Jersey	*	1
New York	11	5
North Carolina	8	6
Ohio	18	3
Oklahoma	19	7
Pennsylvania	11	5
South Carolina	5	3
Tennessee	8	5
Vermont	1	1
Virginia	7	4
West Virginia	3	2
Wisconsin	16	5
TOTAL	275	104

* No analyses available

Analytical Procedures

The analyses were done by a commercial laboratory in West Chester, Pennsylvania, under contract with the U.S. Environmental Protection Agency. The flameless atomic absorption spectrophotometry was applied for the determination of mercury.

Each soil sample, weighed exactly to 1.000 g, was dispersed in nitric acid solution (5 ml concd HNO_3 in 100 ml water). Digestion at 90°C, for approximately 2 hours, took place in the presence of excess potssium permanganate (portions of 1 ml 5% $KMnO_4$ solution were added until purple color persisted) and 2 ml of 5% potassium persulfate solution. After digestion, the mixture was cooled to room temperature and filtered. The filtrate was made to a volume of 100 ml, and 2 ml of sodium chloride-hydroxylamine reagent (12 g each in 100 ml water) was added to reduce the excess permanganate. Stannous sulfate solution (25 g in 250 ml of 0.5N H_2SO_4), 5 ml, was added to reduce mercury ions to elemental mercury, which was swept by an air stream through the absorption cell of the atomic absorption spectrophotometer. The absorptions were measured by peak height, and compared with a calibration curve.

A Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer with Automatic Null Recorder Readout was used for the measurements. The essential instrument conditions were:

Lamp:	Mercury Hollow Cathode Lamp (Westinghouse WL-22847)
Lamp current:	10 mA
Wave length:	253.7 nm
Slit setting:	3
Scale:	× 1
Noise suppression:	2

Precision study, using samples not reported in this paper, indicated a standard deviation of ± 0.16 at a level of 0.35 μg/liter, with recovery average of 87%. The present procedure gave a detection limit of 0.05 μg mercury (or 0.05 ppm per 1-g sample).

Results and Discussion

After testing the distribution form of our data, we found that the data for mercury levels were not normally distributed with both positive skewness and significant kurtosis present. We found, however, that a logarithmic transformation helped the data to approach the normal distribution and to have a symmetric distribution. Shacklette et al. used logarithms to transform their data. They felt that the geometric mean was the best estimate of the central tendency of the data. We have found in our work similar results; therefore, we present both the arithmetic and geometric means. Table 2 shows the geometric means, 95% confidence levels, arithmetic means, the percent of samples that had detectable residues, and the detection range of mercury levels in both cropland and noncropland soils.

TABLE 2.—*Summary of mercury residues detected in surface cropland and noncropland soils of the eastern United States*

	Arithmetic Mean, ppm	Geometric Mean and 95% Confidence Interval, ppm	Range, ppm	Percent of Samples with Detectable Residues
Cropland	0.08	0.063 (0.069-0.058)	<0.05 to 1.06	100.0
Noncropland	0.07	0.054 (0.064-0.046)	<0.05 to 0.40	100.0

Mercury was present in all the samples collected at either a trace level or above. The difference between cropland and noncropland soils were not significant. This was determined from the overlapping confidence intervals. Although these samples were collected at different times, one would not expect mercury levels to change significantly from year to year.

Shacklette et al. have stated (5), "Surficial materials analyzed in this study are ordinarily sampled at a depth of 8 inches. We believe that soils and other regoliths from this depth commonly show little or no effects of surficial contamination that may have occurred." The samples in this study were collected to include possible

contamination of surface soil by pesticides and other pollutants containing mercury. If there had been a significant amount of mercury contamination from manmade sources that had reached soils through airborne or other routes, one would expect our samples to have considerably higher residues than those collected specifically to avoid surface contamination. However, the mercury levels reported in this study are actually lower than those reported by Shacklette et al.

To summarize: in mercury levels of the eastern United States there is no statistical difference between cropland and noncropland soils. The levels detected in this study agree closely with levels detected in similar studies. Actual mean levels of mercury residues in the soils of the eastern United States ranged from 0.05 to 0.10 ppm.

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APPENDIX

Chemical Names of Compounds Discussed in This Issue

BHC	1,2,3,4,5,6-hexachlorocyclohexane, mixed isomers
2,4-D	2,4-dichlorophenoxyacetic acid
DDE	1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethylene
DDT (including its isomers and dehydrochlorination products)	1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane; technical DDT consists of a mixture of the *p,p'*-isomer and the *o,p'*-isomer (in ratio of about 3 or 4 to 1)
DIELDRIN	Not less than 85% of 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8a-octahydro-1,4-*endo-exo*-5,8-dimethano=naphthalene
ENDOSULFAN (THIODAN®)	6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide
ENDRIN	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-endo*-5,8-dimethanonaphthalene
HEPTACHLOR	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4-7-methanoindan
MERCURY	Hg
MIREX	dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[*cd*] pentalene
POLYCHLORINATED BIPHENYLS (PCB's)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorination
TDE (DDD) (including isomers and dehydrochlorination products)	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; technical TDE contains some *o,p'*-isomer also
TOXAPHENE	chlorinated camphene containing 67-68% chlorine

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SUBJECT AND AUTHOR INDEXES

Volume 7, June 1973-March 1974

Preface

Primary headings in the subject index consist of pesticide compounds, the media in which residues are monitored, and several concept headings, as follows:

Pesticide Compounds (listed alphabetically by common name or trade name where there is no common name)

Media and Concept Headings

- Degradation
- Experimental Design
- Factors Influencing Residues
- Food and Feed
- Humans
- Plants (other than those used for food and feed)
- Sediment
- Soil
- Water
- Wildlife

Compound headings are also used as secondary headings under the primary media and concept headings and vice versa. When a particular paper discusses five or more organochlorines or three or more organophosphates or herbicides, the compounds are grouped by class under the media or concept headings; in the primary headings, however, all compounds are listed individually. The specific compounds or elements which have been grouped in various combinations by class for certain papers are as follows:

Organochlorines

- aldrin
- BHC/lindane
- chlordane
- DCBP
- DDE
- DDT
- dieldrin
- endosulfan
- endrin
- heptachlor/heptachlor epoxide
- mirex
- TDE
- toxaphene

Organophosphates

- diazinon
- malathion
- methyl parathion
- parathion

Herbicides

- 2,4-D
- silvex
- 2,4,5-T

In the author index, the names of both senior and junior authors appear alphabetically. Full citation is given, however, only under the senior author, with a reference to the senior author appearing under junior authors.

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